

CHLOROBENZENE AND p-DICHLOROBENZENE

Chlorobenzene is an aromatic liquid at room temperature with a boiling point of 132 °C. p-Dichlorobenzene has a melting point of 53 °C and a boiling point of 174 °C. Commercial production was initiated in 1909 by the former United Alkali Company in England. Hooker Electrochemical Company and Dow Chemical began the U.S. production of chlorobenzenes in 1915. In general, chlorobenzene is less toxic than benzene. The LD₅₀ for chlorobenzene is 2.9 g/kg for rats and 2.8 g/kg for rabbits. The TLV for both components is 75 ppm in air (1).

The sampling and analysis techniques for chlorobenzenes are similar to those for benzene. Solid sorbents are effective for collecting chlorobenzenes, and EPA Method T01 uses Tenax-GC, which has a specific retention volume of 200 L/g for these compounds (2). The use of solid sorbents has also been described by a number of other workers (3-6), and the sorbents are either heat desorbed or solvent desorbed prior to analysis by GC/MS, GC/FID, GC/PID, GC/ECD, or GC/Hall detector. Detection limits are generally in the low ppb range with few interferences and excellent precision (5 to 20% RSD).

Cryogenic trapping also has been explored for chlorobenzene. Pleil and McClenny (7) found that the trap had to be maintained at -150 °C to be effective. EPA Method T03 (8) uses a cryogenic trap and should be an effective sampling technique for chlorobenzene.

Passive dosimeters using charcoal, Tenax-GC, or Porapak R have been described (9,10). The major interference is contamination of the dosimeter, and detection limits of 10 ng/badge were reported.

The methodology for sampling and analysis of chlorobenzene from incineration sources has been well developed using the VOST (11). This system could be adapted to other sampling needs and allows several samples to be pooled to obtain improved levels of detection.

The monitoring of chlorobenzene in ambient air and from specific pollution sources appears to be well developed. Validation of specific methods requires further study.

Sampling and analysis of p-dichlorobenzene would proceed similar to those for benzene and chlorobenzene. Three basic references are of interest. The EPA Tenax-GC method followed by GC/MS analysis (7) provides low detection limits and excellent selectivity. Cryogenic trapping (8) also could be used. NIOSH Method S281 (12) uses a charcoal absorbent, CS₂ to desorb the dichlorobenzene, and analysis by GC.

The techniques for p-dichlorobenzene need to be validated. Extending analytical detection limits to the ppt level requires further investigation. Although sampling and analysis methods for p-dichlorobenzene exist, more work needs to be done.

References

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TABLE 20. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF CHLOROBENZENE

Method No.	Principle	Potential Interferences	Analytical detection limit	Typical sample volume, L	Minimum detectable concentration	Accuracy & precision	References
1	A. Collection on Tenax-GC B. Thermal desorption into cryotrap C. GC/MS	A. Contamination of Tenax-GC B. Compounds having a similar mass spectrum and GC retention time to chlorobenzene.	1-5 ng	100	0.01-0.05 µg/m ³	20% RSD	1,2
2	A. Collection in cryogenic trap B. GC/FID	A. Requires -150 °C to trap chlorobenzene B. Compounds having a similar GC retention time to chlorobenzene.	1-5 ng	100	0.01-0.05 µg/m ³	5% RSD	8
3	A. Passive sampling on charcoal, Tenax-GC, or Poropak R B. GC/LCD/Heil/PID	A. Contamination of sorbent B. Compounds having a similar GC retention time to chlorobenzene	10 ng/hadge	NA	NA	NA	9,10
4	A. Collection on charcoal B. CS ₂ desorption C. GC/FID	A. Water B. Compounds having a similar GC retention time to chlorobenzene	1-5 ng per Injection	10	1.83 x 10 ⁻⁵ µg/m ³ b	6% RSD	6

^a Minimum detectable concentration $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$ unless otherwise stated.

^bThis is the lower limit of the validated range as given in reference 6 and is not necessarily the lower limit of detection.

TABLE 21. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF p-DICHLOROBENZENE

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum ^a detectable concentration	Accuracy & precision	References
1	A. Collection on Tenax-GC trap B. Thermal desorption into a cryotrap C. GC/MS	A. Isomers of dichlorobenzene B. Compounds having similar mass spectrum and GC retention time to p-dichlorobenzene	1-5 ng	100	0.01-0.05 µg/m ³	20% RSD	2
2	A. Collection on a cryogenic trap B. GC/FID	A. Isomers of dichlorobenzene B. Compounds having a similar GC retention time to p-dichlorobenzene	1-5 ng	1	1-5 µg/m ³	5% RSD 10% accuracy	8
3	A. Charcoal B. CS ₂ desorb C. GC/FID	A. Water B. Compounds with similar retention times	1-5 ng per injection	3	1.83 x 10 ⁵ µg/m ^{3b}	6% RSD	12

$$^a \text{ Minimum detectable concentration } \left(\frac{\mu\text{g}}{\text{m}^3} \right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}} \text{ unless otherwise stated.}$$

^b This is the lower limit of the validated range as given in reference 12 and is not necessarily the lower limit of detection.

XYLENES

Xylenes are C-8 benzene homologues with the molecular formula C_8H_{10} . The term mixed xylenes refers to a mixture of ethylbenzene and three xylene isomers. Boiling points of the mixed xylenes are 144, 139, 138, and 135 °C for o-, m-, and p-xylene and ethylbenzene respectively. All are liquids at room temperature. The xylene isomers are flammable liquids and should be stored in approved containers, away from heat or open flames. Xylenes are not very toxic. The oral LD_{50} for rats is 4000 mg/kg. The 8-h TWA for humans is 200 ppm (1).

Sampling and analysis methods for xylene are similar to those for benzene and chlorobenzene. Four methods are of particular interest. EPA Method T01 using Tenax-GC sampling with GC/MS detection (2) provides low detection limits and excellent selectivity. EPA Method T03 uses cryogenic trapping and is an alternative to sorbent trapping (3). NIOSH Method S138 absorbs the analyte on charcoal and uses CS_2 to desorb the sample (4). CARB Method A.D.D.L. 001 collects samples in Tedlar bags and then concentrates a sample onto Tenax-GC (5).

The techniques for xylene need to be validated. If detection limits in the ppt range are necessary, further research will be required.

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TABLE 22. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF XYLENES

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volumes, L	Minimum ^a detectable concentration	Accuracy and precision	References
1	A. Collection on Tenax-GC B. Thermal desorption into a cryogenic trap C. GC/MS	A. Structural isomers B. Compounds with similar retention time to xylenes	1-5 ng	130	0.008-0.04 µg/m ³	20% RSD	2
2	A. Collection in a cryogenic trap B. GC/FID	A. Compounds with similar retention times	1-5 ng	1	1-5 µg/m ³	5% RSD 10% accuracy	3
3	A. Collection on charcoal B. CS ₂ desorption C. GC/FID	A. Water B. Compounds with similar retention times	1-5 ng per injection	12	2.18 × 10 ⁵ µg/m ^{3b}	0.6% RSD Accuracy 2%	4
4	A. Collection in a Tedlar bag B. Concentration of air sample onto Tenax-GC C. Thermal desorption into a cryogenic trap D. Determination by capillary column GC/MS	A. Compounds having a similar mass spectrum to xylenes and similar GC retention time B. Contamination of Tenax-GC cartridge with compound of interest C. Adsorption onto the walls of the Tedlar bag	0.8 ng	2	0.4 µg/m ³	NA	5

^aMinimum detectable concentration $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, (ng)}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$ unless otherwise stated.

^bThis is the lower limit of the validated range as given in reference 4 and is not necessarily the lower limit of detection.

NITROBENZENE

Nitrobenzene ($C_6H_5NO_2$) is a pale-yellow liquid at room temperature with an odor resembling that of bitter almonds. Its melting point is 6 °C, and its boiling point is 211 °C. Nitrobenzene is very toxic. The TLV is 1 ppm (5 mg/m^3). It is readily absorbed by contact with skin or by inhalation of the vapor. It converts hemoglobin to methemoglobin and cyanosis appears when the methemoglobin level reaches 15%. Chronic exposure can lead to spleen and liver damage (1).

Sampling and analysis of nitrobenzene would proceed similar to those for benzene and chlorobenzene. Four references are of interest. EPA Method T01 uses Tenax-GC sampling followed by GC/MS analysis (2) and provides low detection limits with excellent selectivity. Brown (3) has also investigated Tenax-GC as a sorbent for nitrobenzene. Cryogenic trapping with EPA Method T03 (4) also could be used. NIOSH Method S217 (5) uses a silica-gel adsorbent and methanol to desorb the nitrobenzene.

The techniques for nitrobenzene need to be validated. Methods needed to obtain detection limits in the ppt range, if necessary, also need investigation. Although sampling and analysis methods for nitrobenzene exist, more work needs to be done.

References

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TABLE 23. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF NITROBENZENE

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volumes, L	Minimum ^a detectable concentration	Accuracy and precision	References
1	A. Collection on Tenax-GC B. Thermal desorption into a cryotrap C. GC/MS	A. Contamination of Tenax-GC B. Compounds having a similar mass spectrum and GC retention time to nitrobenzene	1-20 ng	100	0.01-0.2 µg/m ³	20% RSD	2,3
2	A. Collection on silica gel B. Methanol desorption C. GC/FID	A. Water B. Compounds having a similar GC retention time to nitrobenzene	1-5 ng per injection	55	3.11x10 ³ µg/m ^{3b}	6% RSD	5
3	A. Collection in a cryogenic trap B. GC/FID	A. Possible ice formation in trap B. Compounds having a similar GC retention time to nitrobenzene	1-5 ng	1	1-5 µg/m ³	5% RSD 10% accuracy	4

^aMinimum detectable concentration $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limits, ng}}{\text{Typical sample volume, L}} \times \frac{1 \mu\text{g}}{1 \text{ m}^3} \times \frac{1 \text{ m}^3}{1000 \text{ L}}$ unless otherwise stated.

^bThis is the lower limit of the validated range as given in reference 5 and is not necessarily the lower limit of detection.

PHENOL AND CRESOL

Phenol is a white crystalline compound with a characteristic odor. Its melting point is 41 °C, and it boils at 182 °C. Cresols (hydroxy toluenes) have a characteristic odor. o-Cresol, m-cresol, and p-cresol melt at 31, 12, and 35 °C respectively. Phenol is toxic and has a TLV of 5 ppm (19 mg/m³). Cresols have similar toxicities and have TLVs of 5 ppm (22 mg/m³) (1).

Phenols and cresols constitute a category and so may be discussed together. Greist et al. (2) used Tenax-GC sampling and GC/MS analysis to analyze cresols. NIOSH Method Sl67 (3) uses silica-gel sampling, extraction with acetone, and GC/FID detection. Method S330 (4) uses a sodium hydroxide solution in a bubbler to trap the acidic compounds. All of these methods provide detection limits in the low µg/m³ range and provide good accuracy (<10%) and precision (<10% RSD).

The extension of the techniques to low levels (ppt) would require further development and validation. The determination of the compounds in air has not been studied to the extent that benzene and other aromatic compounds have been examined.

References

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TABLE 24. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF PHENOLS AND CRESOLS

Method No.	Analyte	Principle	Potential interferences	Analytical detection limit	Typical sample volumes, L	Minimum ^a detectable concentration	Accuracy and precision	References
1	Phenols Cresols	A. Collection on Tenax-GC B. GC/MS	A. Contamination of Tenax-GC B. Compounds with similar mass spectrum and GC retention time	1-5 ng	NA	NA	20% RSD	2
2	Phenol	A. Collection in a NaOH bubbler B. GC/FID	Water	1-5 ng per injection	100	$9.46 \times 10^3 \mu\text{g/m}^3$ ^a	7% RSD	4
3	Cresols	A. Collection on silica gel B. Acetone desorption C. GC/FID	Water	1-5 ng per injection	20	$1.05 \times 10^4 \mu\text{g/m}^3$ ^b	7% RSD	3

^aThis is the lower limit of the validated range as given in reference 4 and is not necessarily the lower limit of detection.

^bThis is the lower limit of the validated range as given in reference 3 and is not necessarily the lower limit of detection.

C. Sampling and Analysis Methods for Semivolatile and Nonvolatile Aromatic Compounds

The determination of semivolatile and nonvolatile aromatic compounds has been studied for many years. Sampling methods include collection on glass-fiber filters (1), membrane filters (2), and polyurethane foam (PUF) (3) using high-volume samplers. High-volume samplers collect air samples at rates varying from 0.2 to 1.7 m³/min depending on back pressure. The more volatile compounds such as low-molecular-weight PAHs, PCDDs, PCDFs and PCBs require a sorbent backup to the particulate filter collection. Tenax-GC (4), XAD-2 (5), and the Source Assessment Sampling System (8) have been used to collect samples. The analytical methods in use are based on GC with FID, ECD, NPD, FPD, or MS detection. HPLC with UV or fluorescent detection has been used for PAH analysis. These compounds are frequently found as part of complex mixtures and often require cleanup prior to analysis. HPLC, TLC, open-column chromatography, and solvent partitioning are popular methods of cleanup.

1. Sampling methods

a. High-volume sampling method

High-volume sampling methods are the methods of choice for ambient-air monitoring. The measurement of PAHs can often be accomplished by using a glass-fiber filter to collect particulate and extracting the filter to begin the sample workup. Most high-volume samplers can collect up to 1.7 m³/min when only a glass-fiber filter is used. The more volatile PAHs have a high enough vapor pressure to breakthrough a simple glass-fiber filter. These require a sorbent back-up such as XAD-2 or Tenax-GC. PCDDs, PCDFs, and PCBs may be collected on a PUF filter with a high-volume sampler. EPA Method T04 describes collection of PCBs with a PUF filter. The flow rates are generally limited to <1 m³/min because of the high back pressure created by the PUF plugs.

b. Source sampling method

Source sampling methods generally use sampling trains such as the EPA Modified Method 5 (MM5) train or the Source Assessment Sampling System (SASS). These samplers consist of a probe for stack sampling, a particulate collection system, and sorbent cartridges with the capability of sampling from 4 to 30 dry standard cubic meters of stack gas over a sampling period of 3 to 5 h.

2. Sample workup

Samples taken with high-volume samplers and associated with particulates often require cleanup prior to the final analysis step. This can involve simple liquid-liquid partitioning to separate a sample into acid, base, and neutral fractions or more elaborate TLC and HPLC fractionations. These steps result in less complicated sample fractions but more samples to be analyzed. Depending on the degree of characterization of the sample required, more or less sample workup may be necessary.

3. Analytical methods

The analysis of PAHs uses many different analytical techniques. The two of most interest involve GC with FID or MS detection and HPLC with fluorescence detection. These methods can give detection limits in the pg/m^3 range.

The analysis of PCDDs and PCDFs is generally based on GC/MS with selected-ion monitoring. GC columns have been developed which will separate most PCDD and PCDF isomer groups. Detection limits below 1 ppb have been reported.

The analysis of PCBs is usually based on GC/ECD although GC/MS is being more widely used. EPA Method TO4 allows the detection of PCBs in the ng/m^3 region.

Research in the analysis of PAHs has also used room-temperature phosphorescence, Shpölski fluorescence, laser-induced fluorescence, and MS/MS. PCDDs, PCDFs, and PCBs have been studied by high-resolution MS, MS/MS, and negative chemical ionization MS. LC/MS is a method which may be applicable to all three classes of compounds.

Individual discussions for the specific compounds of interest follow this discussion.

References

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POLYCHLORINATED BIPHENYLS

Polychlorinated biphenyls (PCBs) were first manufactured commercially in 1929. The sole producer in the United States was Monsanto Industrial Chemicals Company under the trade name "Aroclor." The various Aroclor products that have been marketed include Aroclor 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262, and 1268. The latter two digits indicate the percent chlorine in each formulation except 1016, which contains 41% chlorine. PCBs have been used in a variety of commercial and industrial products including transformers, capacitors, paints, inks, paper, plastics, adhesives, sealants, and hydraulic fluids (1).

The toxicity of PCBs is of particular concern because they are persistent in the environment. PCBs are lipophilic, have been found in human and wildlife adipose tissue, and have been implicated as carcinogens in laboratory studies in mammals (2).

Numerous methods for the determination of PCBs in air have been developed. Many of them use a high-volume sampler for sampling and GC/ECD for analysis.

Margeson (2) reviewed the methods available in 1976. Many collection techniques have been tried. Liquid adsorption using ethylene glycol or toluene to collect PCBs has been reported. Liquid phases coated on solids have also been used to collect PCBs. The phases have included silicone oil on nylon, glycerine on Florisil, cottonseed oil on glass beads, and paraffins on chromosorb. Solid sorbents, including florisil and polyurethane foam (PUF) plugs, were discussed in the review as collection methods for PCBs. The analysis method generally used GC/ECD or GC with microcoulometric detectors. Other workers have used high-volume samplers with PUF plugs (3-5) and in some cases solid sorbents (5-11) to collect the more volatile PCB congeners. Interferences from contamination of glassware and from some pesticides are possible. Limits of detection below 1 mg/m³ were generally found. Good precision (<10% RSD) but variable recoveries (24 to 130%) were found in both ambient air monitoring and source monitoring.

If only total PCBs are to be measured, the sample may be perchlorinated (12,13) prior to analysis by GC/ECD. This eliminates interferences from most sources unless the sample contains biphenyl.

Source sampling using an EPA Modified Method 5 (MM5) sampler was performed during the trial burns of PCBs aboard the M/T Vulcanus (8). Detection limits in the 50 to 200 ppb range with recoveries of 24 to 130% were measured.

The methods for monitoring PCBs appear to be well developed. The use of a solid sorbent to collect low-molecular-weight PCBs behind a PUF plug in a high-volume sampler would provide an adequate sample. GC/ECD or microcoulometric detection provides low limits of detection. In some instances GC/MS may be needed to analyze the PCBs if interferences are present.

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TABLE 26. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYLS

Method No.	Principle	Potential Interferences	Analytical detection Limit	Minimum detectable amount in air	Accuracy and precision	Reference
1	A. Collection on Chromasorb 102 B. GC/LCD	NA	NA	NA	Recovery 66-107%	7
2	A. Collection on Florisil B. Hexane elution C. GC/LCD	A. DOL B. DOL	0.032 ng per injection	10 $\mu\text{g}/\text{m}^3$	4% RSD	9
3	A. Collection on Florisil B. Hexane elution C. Perchlorination D. GC/LCD	Biphenyl	0.032 ng per injection	10 $\mu\text{g}/\text{m}^3$	4% RSD	13
4	A. Collection on Cellulose Membrane B. Petroleum ether elution C. GC/LCD	Compounds with similar retention time	NA	322 $\mu\text{g}/\text{m}^3$	6% RSD	14
5	A. Collection on XAD-2 B. Extraction with CCl_4 C. GC/PID	NA	0.01-0.05 ng per injection	monochloro 3 $\mu\text{g}/\text{m}^3$ dichloro 4 $\mu\text{g}/\text{m}^3$ trichloro 6 $\mu\text{g}/\text{m}^3$ tetrachloro 7 $\mu\text{g}/\text{m}^3$ pentachloro 9 $\mu\text{g}/\text{m}^3$ hexachloro 15 $\mu\text{g}/\text{m}^3$	NA	10
6	A. Collection on glass-fiber filters and Tenax-GC B. GC/LCD	NA	<1 ng	<0.0001 $\mu\text{g}/\text{m}^3$	NA	11
7	A. Collection with high-volume samples on PUF filters B. GC/LCD	A. Compounds with similar retention time B. Glassware contamination	<1 ng	<0.001 $\mu\text{g}/\text{m}^3$	Recovery 36-94%	3
8	A. Liquid adsorption in ethylene glycol or toluene B. Silicone oil on nylon, silicone oil on ceramic beads, 5% glycerine on Florisil, cottonseed oil on glass beads, or paraffin on Chromasorb C. Collection on Florisil or PUF filters D. GC/LCD/microcoulometric	See review article for Interferences	NA	NA	NA	2
9	A. Collection on PUF filter B. Perchlorination C. GC/LCD	Biphenyls	<1 ng	0.001 $\mu\text{g}/\text{m}^3$	NA	12
10	A. Collection on PUF filters B. GC/LCD	Volatile PCBs collected better on Tenax-GC or XAD-2	<1 ng	NA	NA	4,5,6
11	A. Collection on HHS train B. GC/LCD	NA	<1 ng	50-200 ppb	24-130% recovery	8

of the references listed.

POLYNUCLEAR AROMATIC HYDROCARBONS

Polynuclear aromatic hydrocarbons (PAHs) may be the most widespread environmental contaminants. Combustion processes involving carbon and hydrogen produce PAHs, and many are naturally present in vegetation and fossil fuels. Many PAHs are known to be carcinogenic or cocarcinogenic (the result of oxidative reactions in the body). The ability to detect and quantify low levels of the various classes of PAHs is important.

The sampling and analysis of PAHs in air has been studied by numerous workers. This review covers some of the more recent research on air methodology.

The sampling of ambient air for PAHs generally involves high-volume samplers. High-molecular-weight PAHs (three or more rings) are collected efficiently on glass-fiber (1-9) or membrane (10-12) filters or on polyurethane foam (PUF) plugs (13-17). Low-molecular-weight PAHs require another collection medium such as Tenax-GC (18,19), XAD-2 (20), or Florisil (21). The sampling capacity of the materials is in the hundreds to thousands of cubic meters of air for most compounds (15).

Lee and Wright (22) reviewed GC techniques for the analysis of PAHs with numerous detectors (FID, ECD, NPD, FPD, MS). HPLC, with UV or fluorescence detection, has been applied with excellent results (4,5,13,14,15,17,23-28) by many researchers. Room-temperature phosphorescence (29-30), TLC with GC/FID (1) or MS/MS (3) or UV fluorescence (3,12) detection, laser-induced fluorescence (25), and Shpölskii fluorescence (26) have also been studied as cleanup and analysis techniques for PAHs.

In many cases, the high sampling volumes and specific analysis techniques allow picogram (pg/m^3) limits of detection (31). Stray et al. (24) used liquid CO_2 extraction, HPLC cleanup, and capillary GC/negative-chemical-ionization MS to establish limits of detection of $10 \text{ pg}/\text{m}^3$ for pyrene and $500 \text{ pg}/\text{m}^3$ for benzo(a)fluoranthene in particulate samples. Tanner (31) established a limit of detection of $1 \text{ pg}/\text{m}^3$ for benzo(a)pyrene using a high-volume sample, derivatization, and GC/ECD.

The interferences encountered in the determination of PAHs depend on the sampling and analysis technique. The use of HPLC/fluorescence to analyze PAHs from PUF plug extracts (13,14) allowed the detection of 1 to $5 \text{ ng}/\text{m}^3$ of pyrene, chrysene, perylene, and benzo(a)pyrene, but UV absorbers in the PUF plug can be extracted and may interfere with the determination by causing quenching. The analysis of samples collected on glass-fiber filters may be complicated by the reaction of NO_2 with some PAHs (32,37). Interferences from polychlorinated cyclic hydrocarbons (9), some pesticides (17), and contaminated reagents (12,13) have also been reported.

PAHs are generally associated with the particulates in a sample. Analysis methods for particulate samples have been studied using GC/FID (34,35), GC/NPD (35), GC/PID (36), GC/MS (37,38), HPLC (27), and laser MS (39). Duval and Friedlander (40) used a high-volume sampler and GC/FID to examine PAHs in Los

Angeles. The range was in the low ng/m^3 range for anthracene, benzo(a)pyrene, and coronene.

PAHs can differ greatly in chemical properties. The compounds may contain functionalities which greatly influence the analytical methods required. No single sampling-and-analysis method will be suitable for all PAHs in a particular sample. An ambient-air sample collected on a glass-fiber filter with a solid-sorbent back-up may require numerous fractionation and cleanup steps prior to analysis. These procedures may cause widely varying recoveries and poor precision. A procedure developed by Swenson and Vestor (6) gave recoveries of 53 to 104% and relative standard deviations of 5 to 63% for relatively simple PAHs.

The development of methods for PAHs at low levels in ambient air may be implemented by choosing indicator compounds to represent the different chemical properties of this important group of pollutants. We recommend naphthalene, fluoranthrene, and benzo(a)pyrene as representative unsubstituted PAHs. Substituted PAHs may be represented by nitrofluorene and carbazole. Other PAHs may be chosen as needed for specific sampling-and-analysis needs.

The detection of low levels of PAHs using high-volume samplers and HPLC/fluorescence or GC/MS is well developed. Validation of a method using the indicator compounds suggested above would be required to develop a comprehensive PAH screening technique.

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TABLE 27. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS

Method No.	Principles	Potential interferences	Analytical detection limit	Minimum ^a detectable concentration	Accuracy and precision	References
1	A. Collection on high-volume glass-fiber filter B. ILC cleanup C. GC/FID	NA	1-10 ng per injection	<0.0002 µg/m ³	NA	1
2	A. Collection on PUF filter or Bondapak C ₁₈ cartridge B. HPLC/fluorescence	UV absorbers	0.1-0.5 ng per injection	0.0001-0.0005 µg/m ³	NA	13
3	A. Collection on glass-fiber filter B. HPLC/fluorescence	Efficient for benz(a)pyrene at normal temperatures. PAH stabilized by particulates.	Variable depending on the PAH	NA	NA	4
4	A. Collection on high-volume PUF filter B. GC/FID C. HPLC/fluorescence	A. Greater than 1000-m ³ breakthrough volumes. B. Effective for 2-3 ring PAHs	1-10 ng per injection for FID. Variable depending on the PAH using fluorescence	NA	NA	15
5	A. Collection on high-volume sampler B. Derivatization C. GC/LCD	NA	<1 ng per injection	1x10 ⁻⁵ µg/m ³	NA	31
6	A. Collection on high-volume glass-fiber filter B. HPLC/UV	Non-PAH compounds which absorb UV light	Variable depending on the PAH	0.0001 µg/m ³	NA	5
7	A. Collection of particulates with high-volume sampler B. Collection of volatiles on Tenax-GC C. GC/MS	Mutagenicity study has been conducted	1-20 ng per injection	NA	NA	19
8	A. Collection with high-volume sampler B. Electrostatic precipitation of particulates C. GC/FID	NA	1-10 ng per injection	0.0004 µg/m ³	NA	35
9	A. Collection with high-volume sampler B. GC/FID	1-5 ng/m ³ of PAHs found in Los Angeles	1-10 ng per injection	NA	NA	40
10	A. Collection on high-volume glass-fiber filter B. GC/FID C. GC/MS	NA	1-10 ng per injection for FID 1-20 ng per injection for MS	<0.0001 µg/m ³	5-6% RSD 53-104% recovery	6

(continued)

Method No.	Principles	Potential Interferences	Analytical detection limit	Minimum detectable concentration	Accuracy and precision	References
11	A. Collection on high-volume PUF filter B. GC/MS	NA	1-20 ng per injection	phenanthrene + anthracene methylphenanthrene + methylanthracene fluoranthene pyrene fluorene 2x10 ⁻⁵ µg/m ³ chrysene + benz(a)anthracene + triphenylene 5x10 ⁻⁵ µg/m ³ benzo(a)fluorene 2x10 ⁻⁵ µg/m ³ + benzo(b)fluorene 5x10 ⁻⁵ µg/m ³ benzofluoranthene 2x10 ⁻⁵ µg/m ³ phenylene pyrene benzo(a)pyrene 5x10 ⁻⁵ µg/m ³ + benzo(e)pyrene benzo(ghi)perylene 2x10 ⁻⁵ µg/m ³ + anthracene 5x10 ⁻⁵ µg/m ³ o-phenylene pyrene 2x10 ⁻⁵ µg/m ³	NA	16
12	A. Collection with high-volume sampler B. Florisil cleanup C. GC/MS or GC/MS	NA	1-20 ng per injection	isoquinoline methyl quinoline quinoline acridine ethylquinoline benzoquinoline 1x10 ⁻⁵ µg/m ³ 1x10 ⁻⁵ µg/m ³ 1x10 ⁻⁵ µg/m ³ 1x10 ⁻⁵ µg/m ³ 1x10 ⁻⁵ µg/m ³ 1x10 ⁻⁵ µg/m ³	NA	23
13	A. Collection on PUF filter of chlorinated PAHs with a Nutech sampler B. GC/MS using SIM	Pesticides with similar ions	<0.05 ng per injection	<0.0003 µg/m ³	97-100% recovery	17
14	A. Passive sampling on a paper filter B. Room-temperature phosphorescence	NA	0.001-0.6 ng per paper	NA	NA	30

Table 27 (cont. Inued)

Method No.	Principles	Potential interferences	Analytical detection limit	Minimum ^a detectable concentration	Accuracy and precision	References
15	A. Collection on high-volume sampler B. GC/MS	1 ppm NO ₂ degrades pyrene, BaA, BaP but not phenanthrene or chrysene	1-20 ng per injection	NA	NA	32, 33
16	A. Particulates B. GC/FID/NPD C. GC/MS	NA	1-20 ng per injection	0.5-43 µg/g of soot	NA	34
17	A. Collection of a 0.5 m ³ air sample on a membrane filter B. GC/FID	Compounds with similar retention times	1-10 ng per injection	2 µg/m ³	20% RSD	11
18	A. Collection on glass-fiber filter B. Column chromatography C. UV spectrophotometric determination	Any non-PAH compound that co-elutes with the PAH fraction and is UV absorbing	2-3 µg of benzene soluble PAH's per sample	NA	20% RSD estimated	8
19	A. Collection of 0.5 m ³ of air on a membrane filter B. ILC/fluorescence	Contamination of reagents	0.1 ng per sample	2x10 ⁻⁵ µg/m ³	7% RSD	12

^a From the references listed.

PCDDs AND PCDFs

Few environmental or occupational health issues have received the sustained international attention that has been focused on polychlorinated dibenzo(p)dioxins (PCDDs) and, more recently, polychlorinated dibenzofurans (PCDFs) (1). The public has become familiar with these toxic pollutants because of the use of Agent Orange in Vietnam, the improper disposal of toxic wastes in Missouri and New York, reports of contaminated fish in the Midwest, and the consequences of transformer fires.

The toxicity of PCDDs varies greatly. Table 28 (2) gives toxicity data for several congeners of PCDDs.

The toxicity of PCDFs has not been studied as thoroughly as PCDDs. It is thought that the toxicity of furans is similar to dioxins. The levels of furans in the environment may be even higher than dioxins.

PCDDs and PCDFs are being studied intensely as environmental pollutants. Most of the work has concentrated on water, soil, and sediment analysis. Ambient-air monitoring of PCDDs and PCDFs has not been studied extensively.

Smith et al. (3) used a high-volume sampler to measure tetrachlorodibenzo-p-dioxins (TCDDs) and tetrachlorodibenzofurans (TCDFs) on the roof of an office building after a transformer fire. The TCDDs and TCDFs found in these samples were thought to be the result of dilution of the soot material from the fire with dust particles.

Redford et al. (4) collected PCDDs and PCDFs with a high-volume sampler and analyzed them by GC/MS. Detection limits of around 0.25 ng/dry standard cubic meter (dscm) were quoted. In the same study, 0.5 ng/g of PCDDs in fly ash were detected.

Source sampling has been studied in more depth. Several investigators have used EPA Modified Method 5 samplers (MM5) or Source Assessment Sampling System (SASS) trains to collect PCDDs and PCDFs. In all cases GC/MS has been the method of analysis. Two studies were performed to examine the feasibility of sampling incinerator effluents. DeRoos and Wensky (8) spiked XAD-2 and Florisil sorbents and measured recoveries of $92 \pm 8\%$ and $95 \pm 8\%$ of 2,3,7,8-TCDD respectively. Cook et al. (6) spiked a simulated incinerator stack with 1,2,3,4-TCDD and measured recoveries of $115 \pm 45\%$ with the MM5 and SASS trains. An MM5 train was used to monitor the incineration of PCBs aboard the M/T Vulcanous (5). Detection limits of 2 to 22 ppb for TCDDs and TCDFs were reported using GC/high-resolution MS. An Environmental Standards Workshop (9) held on September 18, 1984, has published a method for PCDD and PCDF using HRGC/HRMS or low-resolution (LR) MS at detection limits of 10 to 100 pg/g in stack effluent. Similarly, an MM5 with GC/MS/SIM gave limits of detection for PCDDs and PCDFs in the 30- to 500-pg/g range.

Rappe et al. (10) used HRGC with electron ionization and negative chemical-ionization MS to measure PCDDs and PCDFs generated in PCB fires. Levels of PCDDs and PCDFs generated a PCB fire in Binghamton, New York, were also studied by Schecter (11).

TABLE 28. ACUTE LETHALITY OF PCDD

Isomeric PCDD, Cl position	LD ₅₀ (μg/kg), guinea pig
2,8	300,000
2,3,7	29,000
2,3,7,8	1
1,2,3,7,8	3
1,2,4,7,8	1,125
1,2,3,4,7,8	73
1,2,3,6,7,8	100
1,2,3,7,8,9	100
1,2,3,4,6,7,8	7,200
1,2,3,4,6,7,8,9	4 x 10 ⁶ (mice)

The methodology for the detection of low levels of PCDDs and PCDFs is an active area of research. Smith et al. (12) have reported ppt quantification of PCDDs and PCDFs. However, the cleanup and concentration of samples to allow specificity and low limits of detection require further study and validation. Sampling methods similar to those used for PCBs may be effective but must be validated. The volatility and solubility of nonpolar solvents of PCDDs and PCDFs decreases as the molecular weight of the PCDDs and PCDFs increases. Collection, extraction, and cleanup methods may be slightly different from one isomer group to another. This class of compounds will require much additional research before validated procedures can be published. The selection of PCDD and PCDF congeners to be representative of the 75 PCDDs and 135 PCDFs isomers should include at least one congener from each isomer group.

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TABLE 29. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF
POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS

Method No.	Principle	Potential interferences	Analytical detection limit	Minimum ^a detectable concentration	Accuracy and precision	References
1	A. Collection with MM5 B. GC/HRMS	A. Pesticides B. PCBs	<1 ng per injection	0.0003-0.003 µg/m ³ of ICDF	24-130% recovery	5
2	A. HRGC B. LRMS/HRMS	A. Pesticides B. PCBs	<1 ng per injection	1x10 ⁻⁵ to 1x10 ⁻⁴ µg/g of combustion product	NA	9
3	A. Collection with MM5 and SASS B. HRGC/HRMS	NA	<1 ng per injection	<1.0x10 ⁻⁶ µg/m ³	115 ± 45%	6
4	A. Spiking XAD-2 + Florisil B. HRGC/HRMS	NA	NA	NA	XAD-2 recovery, 92 ± 8% Florisil recovery, 95 ± 8%	7
5	A. Collection with MM5 on XAD-2 B. GC/MS	NA	≈1 ng per injection	1 µg/m ³	NA	Personal com- munication, Merrill D. Jackson, 1984
6	A. Collection with high- volume sampler B. GC/MS	NA	≈1 ng per injection	0.00025-0.0005 µg/g of fly ash	NA	3
7	A. Collection from PCB fires B. HRGC/EI/NCI/MS	PCBs	NA	<0.0001 µg/m ³	NA	10
8	A. Collection with MM5 B. GC/MS/SIM	A. Pesticides B. PCBs	<1 ng per injection	0.00003-0.0005 µg/g of soot	NA	11

^afrom the reference listed.

D. Aldehydes--Formaldehyde, Acetaldehyde, Acrolein

The determination of aldehydes in air has received considerable attention among environmentalists over the last 10 to 20 years. Consequently, typical levels of several predominant aldehydes have at least been tentatively established. The more volatile aldehydes (i.e., C₁ to C₅ aldehydes) exist primarily in the gaseous state in air (1). The concentration of these aldehydes associated with particulate matter is a small, insignificant fraction (<1%) of their total concentration in air (1). Formaldehyde levels in relatively clean air over isolated regions of the oceans have been found to be 0.2 to 1.0 ppb (2,3). In a rural continental area, concentrations of 0.6 to 1.3 ppb have been found (4). Semirural or light industrial areas with little photochemical smog may exhibit levels between 1 and 5 ppb (4,5). Moderate smog conditions in the California South Coast Air Basin produced levels in the 5- to 15-ppb range (6), and intense smog produced 40 to 150 ppb (1,6). In other urban areas, levels in the range of 10 to 40 ppb are typical (1,7). Levels in residences approach 25 to 107 ppb, concentrations comparable to those found in heavily polluted air (8,9). Levels in diesel exhaust are 5 to 10 times greater than ambient levels. Lipari and Swarin (5) report concentrations of 141 to 491 ppb, and Menzies et al. (10) report 9,800 to 13,200 ppb. Workplace atmospheres have been found to contain about 500 to 2,200 ppb depending on the chemical process involved (5,11).

Considerably less information is available with regard to acetaldehyde levels in air. However, several studies have indicated that acetaldehyde is often found in polluted atmospheres along with formaldehyde. Acetaldehyde levels are usually less than formaldehyde levels. Tanner and Meng (7) found that acetaldehyde levels were 20 to 50% of formaldehyde levels near Brookhaven National Laboratory in New York. In diesel exhaust, Menzies et al. observed that acetaldehyde levels were about 20% of formaldehyde levels. Grosjean and Kok (12) report acetaldehyde levels up to 35 ppb in a study of the California South Coast Air Basin. Typical concentrations, however, were 5 to 10 ppb when formaldehyde levels were 5 to 40 ppb. Kuwata et al. (13) observed 2 ppb of both acetaldehyde and formaldehyde in a Japanese industrial area.

Information regarding concentrations of acrolein in air are even more sparse than that of acetaldehyde concentrations. Altshuller and McPherson (14) reported in a 1963 study that acrolein levels averaged 7 ppb with a maximum of 14 ppb. Changes in these levels were related to changes in formaldehyde concentrations. The acrolein concentrations were typically about 15% of the formaldehyde concentrations. In a much more recent survey of air contaminants in 1978, Pellizzari (15) found acrolein concentrations of about 2 ppb downwind of a waste-disposal site and concentrations from 0.3 to 0.8 ppb downwind of a chemical plant. Acetaldehyde levels at the same sampling sites were usually >10 times higher. Formaldehyde levels were not determined. Cohen and Altshuller (16) reported 7,000 to 8,700 ppb of acrolein in automobile exhausts.

Numerous air-sampling and analysis methods have been developed that are capable of determining aldehydes in ambient air. Most of these are also adaptable to source monitoring. Many have exploited the reactivity of the carbonyl group. Traditional methods have involved the reaction of aldehydes with reagents to form color-absorbing species that are determined spectrophoto-

metrically (17,20). Sampling methods appropriate for these colorimetric analysis methods have often involved collection in absorbing solutions in impingers or bubblers (17,21). At least one colorimetric method has been automated to measure formaldehyde levels continuously (18). More recently, passive samplers based on diffusion or permeation have been adapted to some of these traditional analytical methods (8-9, 22-23). Other analytical methods involve derivatization of aldehydes to form species that can be easily speciated according to each aldehyde and determined by GC (24,25) or HPLC (1,6,7,10,12,26-30,66). Sampling methods amenable to these derivatization analysis methods have involved the use of impingers and solid-sorbent tubes.

Other methods are available that determine aldehydes directly without reaction. These include GC analysis methods in which air samples are injected into the GC column with a gas-sampling loop or syringe (10, 31-33) and methods in which aldehydes are collected in a cold trap or sorbent bed and then thermally transferred to the GC (30-31, 33-34). Other direct methods are based on sophisticated instrumental techniques, involving FTIR (35-36), UV (4), microwave (31,37), and photoacoustic laser spectroscopy (38) and chemiluminescence and laser-induced fluorescence (31).

All methods, both reactive and direct, are summarized in Tables 30 through 32. To allow easy comparison of their relative merits, we have presented information relating to method interferences, the limit of detection, accuracy and precision, sampling capacity, and the stability of samples. A detailed discussion of each method is given separately below for formaldehyde, acetaldehyde, and acrolein.

1. Formaldehyde

a. Spectrophotometric methods for the determination of formaldehyde

(1) Chromotropic acid method/active sampling chromotropic

Of the traditional colorimetric methods for aldehydes, the chromotropic acid (CA) method appears to have been used and evaluated most extensively. In fact, the method is considered reliable enough to have been used in recent years as a reference air-sampling and analysis method in several studies of the comparative reliability of several approaches (1,9,10).

Principle and History of the Method. The CA method is based on the formation of a purple monocationic chromogen. The chromogen results from the reaction of formaldehyde with CA, which is 4,5-dihydroxy-2,7-naphthalene disulfonic acid in a strong sulfuric acid solution. As early as 1935, Eegriew (39) proposed CA as a spot test reagent for identifying formaldehyde in the presence of other aldehydes in organic samples. Bricker and Johnson (40) subsequently published in 1945 a spectrophotometric method for the determination of formaldehyde in aqueous solution. In the early 1950s and 1960s, West and Sen (41) and Altshuller et al. (17) developed and refined air-sampling and CA analysis methods for the determination of formaldehyde in ambient air. Since then, numerous investigators have used or recommended the use of the method in air-pollution studies (17,42), source monitoring (10), indoor-air monitoring (9),

and workplace-air monitoring (43). Summary descriptions of the CA method and modifications of the method are given in Table 30.

Sampling Procedures. The method as originally proposed by Altshuller involved the collection of formaldehyde in air in a standard midget impinger containing 0.1% CA in concentrated sulfuric acid (17). In addition to being very corrosive, the concentrated sulfuric acid also increased the likelihood of negative interferences from alkenes. Alkenes have been observed to react with formaldehyde in the presence of concentrated sulfuric acid (31). Consequently, subsequent refinements specified alternative collection media, including distilled water, 1% (w/v) sodium bisulfite in water, and 0.1% CA in water. Once sampling was complete, aliquots of these collection media were combined with the appropriate reagents for the subsequent absorbance measurements. Of these three alternative media, water and 1% sodium bisulfite have been used more extensively. Sodium bisulfite solution appears to have offered greater utility than has water in the sampling of particularly complex source samples, such as diesel exhaust, presumably because of the limited solubility of many potentially interfering contaminants in the salt solution (10). Menzies reports a 98% collection efficiency for 1% sodium bisulfite (10). Water has been found to be an entirely acceptable sampling medium, however, in less complex samples, such as ambient air or indoor air (9,42). Information concerning differences in formaldehyde collection efficiency between water and sodium bisulfite solution is conflicting (9,42,44). The Intersociety Committee on Methods of Air Sampling and Analysis has suggested that formaldehyde can be efficiently collected in air samples as large as 1,400 L with midget impingers containing water as a collection medium (42). Georgiou et al. report a collection efficiency of >90% for water (44).

Sensitivity, Specificity, and Stability. No matter which sampling medium has been used, the CA method with impinger sampling offers several advantages for application to ambient air and source monitoring. The sensitivity of the method is good, with reported detection limits ranging from 10 to 50 ppb in a 60-L air sample and 2 ppb in a 1,400-L air sample (1,9,10,17,31,39,40,42-44). Another advantage of the method is its selectivity for formaldehyde over other aldehydes. Sleva (45) reported that other saturated aldehydes at levels comparable to formaldehyde present less than 0.01% positive interference while acrolein causes only a few percent positive interference on a molar basis. As noted above, alkenes in general do not cause significant interference when the formaldehyde is collected in water or 1% sodium bisulfite. Furthermore, other potential interferents--alcohols, aromatic hydrocarbons, and phenol--are not expected to interfere unless present in great excess. The purple chromagen formed by reaction of formaldehyde with CA is reasonably stable in solution. A 3% loss occurs after 1 day and a 10% loss after 10 days at room temperature (42).

Accuracy and Precision. Yet another advantage of the method is its accuracy and precision. In an interlaboratory test, analytical results agreed to within 5% for the determination of 1 to 20 µg of formaldehyde (42). One comparative study of the CA method, the MBTH method (see below), and the DNPH/HPLC method (see below) found all three methods equivalent at concentrations near 1000 ppb of formaldehyde in clean air (10). Another research group found reasonable agreement between the CA method and determinations by FTIR for 120 to 320 ppb of formaldehyde in ambient-air samples (1).

(2) Chromotropic acid method/passive sampling

Recently the CA method has been adapted to passive sampling techniques. Although the accuracy and precision has not yet been shown to match that of corresponding impinger methods, the simplicity and portability of passive samples can be greatly advantageous in ambient-air monitoring. Hodges et al. (22) have evaluated a passive sampler comprising a glass tube with one end open to the atmosphere and the other sealed. Inside the tube near the sealed end is placed a glass-fiber filter impregnated with sodium bisulfite. Formaldehyde diffuses to the filter where it is chemically fixed. The collected formaldehyde is desorbed with water and determined by the CA method. The device has been shown to yield a +15% bias relative to the impinger sampling method. Accuracy is also a function of the relative humidity, and at relative humidities above 60%, accuracy is acceptable. The precision of determinations with the device, however, appears to be acceptable. One major advantage of the device is that exposed samples can be stored at ambient temperatures for up to two weeks prior to analysis. But a potential disadvantage is that the device is only practical for determining formaldehyde at ambient air levels if long exposure times are used. For example, the tube must be exposed for one week to reach a limit of detection of 18 ppb. Similar performance has been found with the formaldehyde badge marketed by 3M Company (8). The detection limit (5 ppb/week) is somewhat lower than that for the tube device because of the greater surface area of the sodium bisulfite-impregnated collection pad and the shorter diffusion path length. Once again, accuracy is dependent on the relative humidity. In contrast to the tube sampler, however, low relative humidity (i.e., $\leq 40\%$) causes determinations with the 3M badge to be inaccurate (46). A third passive device, the Pro-Tek badge (8) marketed by Du Pont, is not subject to the effects of relative humidity. This device comprises an aqueous sodium bisulfite reservoir interfaced with a polymer permeation barrier for the "sampling" of formaldehyde. A field test of the device revealed that results were comparable to results obtained with impinger sampling. A limit of detection of 40 ppb/24 h has been reported with the caution that the error in determinations is significant because of high sampler blanks unless sampling times are ≥ 72 h.

(3) Pararosaniline method

Principles and History of Method. Another colorimetric method that has received wide usage is the pararosaniline method as developed by Lyles et al. (18). The principle of the method involves the reaction of formaldehyde in aqueous solution with acid-bleached pararosaniline and sulfite to produce a blue alkylsulfonic acid chromophore with an absorbance maximum near 570 nm (47). As early as 1866, Schiff (48) used the reaction of basic fuchsin--a mixture of rosaniline hydrochloride and pararosaniline hydrochloride--with formaldehyde as a spot test for formaldehyde. It was not until 1956 that West and Gaeke (49) demonstrated the importance of using purified pararosaniline instead of basic fuchsin to enhance color development. Actually, West and Gaeke developed a method for the determination of sulfur dioxide with bleached pararosaniline and formaldehyde as the color-developing reagents. In this method, sulfur dioxide was stabilized in solution by complexation with tetrachloromercurate(II) to form dichlorosulfitomercurate(II). Lyles et al. then adapted the West and Gaeke approach to the highly sensitive determination of formaldehyde. See Table 30 for a summary description of this method.

Sampling Procedures--Active and Passive. In the procedure published by Lyles et al. (18), formaldehyde is sampled by both manual and automated techniques. In the manual approach, formaldehyde is collected in distilled or boiled demineralized water in impingers. After air sampling, aqueous sodium tetrachloromercurate and sodium sulfite are added to the impinger solution. Subsequently, acidified pararosaniline hydrochloride in aqueous solution is added. The solution is mixed thoroughly and should stand for about 15 min for color development. In the automated approach, a dilute aqueous tetrachloromercurate solution and a sodium sulfite solution are continuously mixed and then circulated through an air scrubbing chamber where the formaldehyde is sorbed. On exiting the scrubber, the solution is combined with a stream of pararosaniline solution to develop the color and the intensity of the color is monitored continuously. One minor disadvantage of the manual technique is that the dichlorosulfitomercurate complex is somewhat unstable and must be replaced every 24 h. The automated method generates the complex continuously and, thus, avoids the instability problem.

Recently, Miksch and his co-workers (50) have shown that the use of the toxic tetrachloromercurate(II) solution in the manual or automatic approach is unnecessary if the sulfite is added after the addition of the pararosaniline reagent. They also found it necessary to maintain the mixed sample solutions at 25 °C for 60 min for color development prior to the measurement of absorbance. Miksch and his co-workers also designed a refrigerated field-sampling chamber for sampling with impingers containing water. With the device, 24-h samples (>1000 L of air) can be taken without unacceptable loss of the water-absorption medium. Furthermore, the solution of collected formaldehyde in water has been found to be stable for two weeks under refrigeration. One major disadvantage of the modified pararosaniline approach is that it suffers from interference by sulfur dioxide in the atmosphere, whereas the original method by Lyles et al. does not.

Matthews and Howell (51) have adapted a solid-sorbent sampling procedure to the pararosaniline method. Formaldehyde is collected on 13X molecular sieves, desorbed with water, and then determined by the modified pararosaniline procedure developed by Miksch et al. The solid sorbent facilitates field sampling considerably; however, the coadsorption of water vapor limits air-sampling volumes to about 60 L for a 10-g bed of 13X molecular sieves.

Gammage et al. have reported the use of a passive sampler comprising a reservoir of water with a poly(dimethyl silicone) (PDMS) membrane as a permeation barrier. Formaldehyde in air permeates the membrane and dissolves in the water. The water is then analyzed by the modified procedure of Miksch et al.

Sensitivity. Irrespective of the sampling approach, the sensitivity of the pararosaniline analysis method is an attractive feature with regard to ambient air sampling. Estimates of the limit of detection for impingers and sorbent-tube sampling methods have generally been around 25 ppb of formaldehyde in a 30- to 60-L air sample. Lyles and co-workers (18) reported a detection limit of about 25 ppb in a 30-L air sample. Although the estimate was based on analytical data only, Miksch and co-workers (50) estimated a detection limit of 25 ppb in a 60-L air sample, which corresponds to about 1 ppb in a 1000-L air sample. Matthews and co-workers (51) also report a detection limit of 25 ppb in a 30-L air sample taken with 13X molecular sieves. The passive sampler of

Gammage and co-workers (23) allows a limit of detection of about 25 ppb in 24 h. The continuous analyzer based on the modified pararosaniline method and marketed by CEA Instruments, Inc., has a reported limit of detection of 2 ppb (18).

Specificity. The pararosaniline method is virtually specific for formaldehyde. Lyles and co-workers (18) found that many other aldehydes, including cinnamaldehyde, crotonaldehyde, butyraldehyde, and chloroacetaldehyde, did not give positive responses even when concentrations were as high as 10% by volume. Propionaldehyde and acetaldehyde interfered only slightly with formaldehyde determinations. Miksch and co-workers (50) demonstrated that the following concentrations of other aldehydes gave only a 10% interference when determining 33 μM formaldehyde by their modified pararosaniline method:

- acetaldehyde--220 μM
- acrolein--120 μM
- propionaldehyde--640 μM
- glyoxal--500 μM

Negative interferences with sodium sulfite, potassium cyanide, and hydroxylamine were, however, observed. Formaldehyde forms adducts with sulfite, cyanide, and hydroxylamine that limit the availability of formaldehyde for reaction with pararosaniline. The addition of heavy metal ions, including Hg(II), Cd(II), Ni(II), Fe(II), or Zn(II), were found to greatly reduce these negative interferences by decomposing the adducts. Also the sulfite interference was reduced to insignificant levels by the addition of sodium hydroxide to the sample solution prior to analysis.

Accuracy and Precision. The accuracy of the pararosaniline method has often been demonstrated by comparison to the CA method. In indoor air determinations near 50 ppb, it was found that the modified pararosaniline procedure and the CA methods gave results that were not statistically different at the 95% confidence level (50). The error in individual analyses of spiked solutions was estimated to be 1 to 2% over the range of the method (50). The CEA continuous analyzer demonstrated agreement to within $\pm 3\%$ of results obtained by the CA method with a 1% range of reproducibility in replicate analyses (8). At concentrations from about 25 to 100 ppb, Matthews demonstrated excellent agreement between results obtained with the 13X molecular sieve tube sampler and results obtained by impinger sampling or the CEA analyzer (51). All analyses were performed by the modified pararosaniline procedure. Test results defining the reliability of the permeation sampler of Gammage et al. (22,23) were unavailable.

(4) MBTH method

Principle and History. Another colorimetric method that has received wide usage involves the reaction of formaldehyde with 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH) (19). The azine resulting from this reaction is then oxidized with ferric chloride in an aqueous solution of sulfamic acid to form a blue cationic dye with strong absorption in the range of 628 to 635 nm. Formaldehyde is collected in 0.05% aqueous MBTH and the colored reaction product is developed just prior to analysis.

The method has been used to determine "total" aldehydes (19,31,52). Most other aldehydes demonstrate similar reactivity toward MBTH. However, there are significant differences in molar absorptivity among the reaction products of individual aldehydes (10). The molar absorptivity of the formaldehyde reaction product is about 25% greater than the molar absorptivity of other straight-chain aliphatic aldehydes and about three times the molar absorptivity of branched-chain and olefinic aldehydes. Consequently, the MBTH method is only quantitative when it has been calibrated for an individual aldehyde and when the concentration of that aldehyde in an air sample is predominant relative to the concentration of other aldehydes. The method has found the greatest application in the determination of formaldehyde in air where the concentrations of other aldehydes are much lower than formaldehyde levels (10,19).

Sensitivity, Stability, and Accuracy. The greatest advantage of the method appears to be its sensitivity. Estimates of limits of detection have been as low as 1 ppb in a 720-L air sample or 10 ppb in a 60-L air sample (10,19). Also, the formaldehyde reaction product is stable for >13 days in MBTH solutions. Furthermore, the method is rugged enough to have been adapted to a visual-screening field procedure for indoor air monitoring with a lower limit of detection of about 100 ppb (51). In this application, formaldehyde is collected passively in a water reservoir capped with a PDMS-membrane permeation barrier and subsequently determined by the MBTH method. The analytical method alone has been demonstrated to be accurate in interlaboratory testing. Results in three different laboratories agreed to within 5% over the range of the method (19).

Specificity. The susceptibility of the method to interferences from other aliphatic and olefinic aldehydes is a major disadvantage. Less severe interference also occurs from several compound classes (19,52) including aromatic amines, imino heterocyclies, carbazoles, azo dyes, stilbenes, Schiff's bases, the aliphatic aldehyde 2,4-dinitrohydrazones, and compounds containing the *p*-hydroxystyryl group. In practice, however, few of these compounds are volatile enough or water-soluble enough to present major interferences in air sampling.

(5) J-Acid method

One of the less frequently used colorimetric methods involves the reaction with 6-amino-1-naphthol-3-sulfonic acid (J-acid) to produce a chromophore with an absorbance maximum near 470 nm. As originally proposed by Sawicki (20), formaldehyde is collected in water in an impinger and then an aliquot of the solution is reacted with J-acid. The method is selective for formaldehyde, but high concentrations of other aldehydes will interfere.

Nevertheless, a recent modification of the method makes it potentially applicable to ambient and source air sampling. Bisgaard et al. (54) have developed a method that involves the collection of formaldehyde on Chromosorb W coated with a solution of 0.6% J-acid in concentrated sulfuric acid. The reaction product is desorbed with concentrated sulfuric acid and determined by either of two alternative analysis methods. One is the traditional spectrophotometric approach with a detection limit of about 150 ppb in a 4-L air sample or 50 ppb in a 12-L sample. The other method is a fluorimetric determination with an excitation wavelength of 470 nm and an emission wavelength of 520 nm.

The detection limit of the fluorimetric method is about 13 ppb in a 4-L air sample and about 4 ppb in 12-L sample.

An important improvement of the fluorimetric method over the original spectrophotometric method is that interference problems have been reduced significantly. Acetaldehyde and propionaldehyde do not exhibit any interference with the fluorimetric method. Acrolein gives a response that is only 5 to 7% of the response for an equimolar amount of formaldehyde. An additional advantage is that formaldehyde samples collected on the tubes are stable for ≥ 10 days at room temperature.

Fluorimetric and spectrophotometric accuracy and precision of the solid-sorbent sampling approach with both analysis techniques has been found to be acceptable in laboratory testing in the range of about 175 to 630 ppb. The two methods have been found to agree to within 5%, and the average recovery of results with both techniques has been observed to be $101 \pm 8\%$ (95% confidence limits) when compared to standard atmospheres prepared with permeation tubes.

One disadvantage of the solid-sorbent sampling approach, however, is the limitation on the capacity of the tube for formaldehyde at high relative humidity (RH). The capacity is 47 μg of formaldehyde for each gram of sorbent in dry air but falls to 9 μg of formaldehyde for each gram of sorbent at 70% RH.

b. Chromatographic methods for the determination of formaldehyde

(1) DNPH/HPLC method

Principle and History. One derivatization method involves the condensation reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine (DNPH) to form the corresponding hydrazones (1,5,7,10-13,27-30,66). Each individual aldehyde or ketone produces a unique compound that can then be determined by gas chromatography (GC) or high-performance liquid chromatography (HPLC). Historically, investigators have found that HPLC separates the isomeric hydrazones better than does GC (7). Thus, greater emphasis has been given to the HPLC approach, and we will limit our discussion to DNPH methods involving this approach.

The primary advantages of determining formaldehyde in air by the DNPH/HPLC approach include acceptable specificity that makes the methods almost interference free for air samples, sensitivity that allows determinations of ambient-air levels in clean or polluted air, and accuracy and precision comparable to or better than that offered by alternative techniques. Some minor disadvantages are related to the instability of DNPH solutions and the contamination of samples with extraneous formaldehyde. Both advantages and disadvantages are discussed in greater detail below.

DNPH Sampling Techniques and Collection Efficiencies. Several sampling schemes have been developed for the DNPH/HPLC approach. Most of these have included impinger sampling, but others have used a rotating flask containing coated raschig rings or a solid-sorbent tube. The collection solvents in the methods involving impingers have been acidified aqueous solutions of DNPH (1,10,12, 27,30), DNPH in acidified acetonitrile (7,29), or a two-phase mixture

of hydrocarbon solvent and an aqueous acidified DNPH solution (1,12,28,66). All solutions have been acidified primarily to promote the protonation of the carbonyl (1,26). The DNPH/acetonitrile solution will collect formaldehyde at concentrations of ≤ 150 ppb with 80% efficiency in 30-L air samples, but an ice bath is required to maintain this sampling efficiency (7).

The most novel liquid-phase sampling device that has been used with the DNPH/HPLC approach is that developed by Lowe et al. (27). The device comprises a custom-made glass flask packed tightly with raschig rings that are continually rotated into a pool of DNPH and sulfuric acid in aqueous solution. With this device the collection efficiency for formaldehyde has been found to be 95 to 100% for air-sampling rates of ≤ 50 L/min. The device was routinely operated at 40 L/min for sampling times up to 1 h, corresponding to 2-m^3 air volumes.

Several types of DNPH sorbent tubes have been applied to the collection of formaldehyde in air. Grosjean and co-workers (55) have coated 20-mesh glass beads with phosphoric acid saturated with DNPH and with a small amount of poly(ethylene glycol) added to promote the formation of a viscous film on the beads. Unspecified amounts of this sorbent have been packed into 100 x 6-mm glass tubes for sampling. The collection efficiency at a 1-L/min sampling rate has been found to average 90% for about 100 ppb of formaldehyde in air maintained at 40 to 50% RH but has been observed to fall to $\approx 25\%$ at $< 1\%$ RH.

Beasley et al. (11) have designed a sorbent tube containing silica gel coated with DNPH and hydrochloric acid (55). This type of tube has been found to be $> 90\%$ efficient for the collection of over 100 μg of formaldehyde in a 20-L air sample at a sampling rate of 0.1 L/min. Humidity has been observed to have little effect on collection efficiency or the capacity of the tube for formaldehyde. However, collection efficiency has been found to be highly dependent on the tube preparation procedure. The order of the addition of reagents is especially critical.

Kuwata and co-workers (13) have found the Sep-Pak C_{18} cartridge (Waters Associates, Milford, MA) coated with DNPH and phosphoric acid to be effective in sampling a variety of aldehydes, including formaldehyde. These tubes have demonstrated better collection efficiencies than those produced by Fung and Grosjean (26) and are less difficult to prepare than those of Beasley et al. (11). In taking ambient air samples with the modified Sep-Pak C_{18} cartridges, the collection efficiencies have been found to be $> 95\%$ for < 2 ppb concentrations of C_1 to C_3 aldehydes in 100-L air volumes and at sampling rates of 0.7 to 1.2 L/min. At concentrations of about 900 ppb of formaldehyde and 500 ppb of acetaldehyde, the collection efficiency has been found to the 100% in 2- to 10-L air samples collected at 0.5 to 1.5 L/min. Furthermore, humidity has no effect on collection efficiencies.

Lipari and Swarin (5) have recently reported the design and evaluation of another sorbent tube. Florisil (60 to 80 mesh) in Thermo-sorb/F air-sampling cartridges (Thermo Electron Corporation, Waltham, MA) is coated with DNPH alone. At 1 L/min, the collection efficiency for formaldehyde at a concentration of 92 ppb in 1-m^3 air samples is $> 95\%$. As with the coated Sep-Pak C_{18} cartridge, relative humidity demonstrates no effect on sampling efficiency.

Interferences. The specificity of the DNPH derivatization reaction for carbonyl compounds and the resolution of derivatives by HPLC make the determination of formaldehyde by the DNPH method generally free of interferences (1,11). The formaldehyde derivative is easily separated from the derivatives of acetaldehydes, higher aldehydes, and, also, ketones. Although high concentration of oxidants (e.g., 0.1% ozone in air) will degrade DNPH and its derivatives, Lowe et al. (27) have observed that concentrations of ozone near 100 ppb, which are typical of ambient air, did not interfere. Furthermore, Lipari and Swarin also have found that nitrogen dioxide at concentrations of from 137 to 550 ppb in air does not interfere with the determination of 77 ppb of formaldehyde samples on their DNPH/Florisil tube samples.

The potential interference of sulfur dioxide in techniques using liquid collection media is avoided because the collection solutions are strongly acidic. Sulfur dioxide dissolves in aqueous solution to form sulfurous acid, which dissociates to yield sulfite and bisulfite ions. Bisulfite is known to react with formaldehyde, but the resulting adduct is unstable under strongly acidic conditions (27). Lowe et al. (27) have observed that 90 ppb of sulfur dioxide does not interfere with determinations when the pH of the collection solution medium is 3. Lipari and Swarin (5) have also found that 100 ppb of sulfur dioxide in air has had no effect on the determination of 92 ppb of formaldehyde in their DNPH/Florisil tube sampler. The DNPH derivatives are apparently stable to mixtures of reactive gases in the ambient air. Grosjean (1) has found that, once formed, the dinitrophenyl hydrazone of acetaldehyde is stable to ≈ 15 ppb of nitrogen dioxide, ≈ 200 ppb of ozone, and undetermined concentrations of sulfur dioxide, peroxyacyl nitrates, free radicals, and other pollutants in urban air. Presumably the formaldehyde hydrazone is as stable to reactive atmospheric contaminants.

There are at least two potential causes of interferences for the DNPH approach. One of these involves reagent contamination and will be discussed in depth in the paragraph below describing sensitivity. Briefly, the contamination of the DNPH and other reagents with formaldehyde limits analytical sensitivity to levels at least tenfold higher than could be attained otherwise (1,5,27). The second potential cause involves degradation products of the DNPH that can interfere with formaldehyde determinations. Lowe et al. (27) found that DNPH solutions deteriorated in an unpredictable manner to give two degradation products. One of these products sometimes reached levels high enough to interfere with formaldehyde determinations. Storage in sealed Pyrex bottles at 4 °C reduced the decomposition significantly. In most methods involving impinger sampling, the possibility of interference by DNPH degradation products has been avoided by the extraction of the aqueous acid DNPH collection media with a hydrocarbon solvent. Apparently, little DNPH and none of its degradation products are extracted along with the aldehyde hydrazones.

Potential interference from water vapor in ambient air was mentioned above in the discussions of collection efficiency. As pointed out there, humidity has demonstrated an effect on formaldehyde collection efficiency with only one type of sampler, a tube sampler containing DNPH, phosphoric acid, and polyethylene glycol on glass beads (55). High humidity enhanced the sorption of formaldehyde but the compound was not sorbed well at low humidity.

Sensitivity. Many of the DNPH/HPLC methods have demonstrated adequate sensitivity for the determination of formaldehyde at ambient-air levels. Whether the sampling technique involves a liquid collection medium or a sorbent tube, most methods are capable of quantifying levels of <1 to <3 ppb in 30- to 100-L air samples (1,5,7,10-33,27-30,66). Furthermore, lower levels can usually be determined by increasing the sampling volume as long as the breakthrough volume is not exceeded. Thus, with the method developed by Lowe et al. (27) one can determine 0.2 ppb of formaldehyde in a 2-m³ air sample.

Lower levels could be determined if method blanks could be lowered. For most methods, the instrumental detection limit is on the order of <0.1 ng/mL of formaldehyde in the final extract or solution analyzed whereas method blanks correspond typically to 1 to 60 ng/mL (5,12,27). Extraneous sources of formaldehyde include the DNPH reagent, solvents (including water), plastic labware, contaminated glassware, and exposure of samples to ambient air.

Although most investigators have attempted to purify commercially available DNPH by recrystallization or extraction, traces of the formaldehyde derivative persist. Lipari and Swarin (5) report a contamination level equivalent to 2 ng of formaldehyde in each milligram of DNPH even after two recrystallization steps. Thus, in most DNPH methods involving sorbent tubes and in nonaqueous impinger methods, DNPH appears to be a primary source of high blank values. For example, if we assume a contamination level of 2 ng/mg, the tube developed by Beasley et al. (11) contributes 250 ng to the blank and corresponds to a formaldehyde concentration of 125 ng/mL in the acetonitrile extract, which, in turn, would correspond to about 10 ppb in the recommended 20-L air sample volume. In fact, Beasley and his co-workers did experience unusually high blanks (~1000 ng/mL) that limited accurate determinations to concentrations on the order of 80 ppb. Beasley et al. also attributed another primary source of contamination to Bakelite vial caps.

Water is a primary source of extraneous formaldehyde in those methods involving aqueous collection media. Lowe et al. (27) found that formaldehyde levels could be minimized by passing the water through a dual ion-exchange high-purity water system. However, even after this treatment, contamination levels were still 0.5 to 5 ng/mL. In the rotating-flask sampler used by Lowe et al., water would be expected to contribute the major portion of the 3.5-ng/mL blank value observed. Also, in the impinger methods of Grosjean et al. (1,12,26,55), Menzies et al. (10), Riggin (28,66), and Harris et al. (30), water would be expected to contribute enough formaldehyde to produce blank concentrations of from 1 to 60 ng/mL. Formaldehyde may also be absorbed from background air into sampling solution prior to actual air sampling. Consequently, Riggin (28,66) suggested that DNPH solutions be prepared no sooner than 48 hours before sampling and doubly sealed within two airtight containers until sampling.

Accuracy and Precision. Although the DNPH/HPLC method has not been evaluated as thoroughly as have many of the spectrophotometric methods previously discussed, a number of research groups have attempted validation for formaldehyde determinations with reasonable success. Grosjean and co-workers (1,12,26,55) have recovered an average of 96% of spikes into impinger solutions of aqueous, acidic DNPH for 4- to 19-ng quantities of formaldehyde with a relative

standard deviation (RSD) of 4.2%. The overall method including impinger sampling, solvent extraction and concentration, and HPLC analysis compared well with reference methods in determining formaldehyde levels in the range of 120 to 320 ppb. Regression analysis of the DNPH method versus the CA method or the FTIR approach gave slopes near unity. Menzies et al. (10) found that the analysis of diesel exhaust for formaldehyde by the DNPH method with aqueous, acidic DNPH impinger sampling was statistically equivalent to the CA and MBTH methods at concentrations around 1 ppm with RSDs from 3.0 to 13.6%. The DNPH method gave values within $\pm 10\%$ of the theoretical value in laboratory testing. Riggins (28,66) stated that recoveries for several aliphatic aldehydes including formaldehyde from impinger solutions of isooctane and aqueous, acidic DNPH solutions are generally $>75\%$ with RSDs of 15 to 20% for replicate air samples. Tanner et al. reported linear calibration curves in the range of 30 to 150 ppb of formaldehyde samples in standardized atmospheres with impinger solutions containing DNPH and sulfuric acid in acetonitrile. Singh et al. (29) reported good correlation of the CA procedure and the HPLC analysis of impinger solutions of DNPH and sulfuric acid in acetonitrile. However, to obtain accurate results, the authors heated the solutions for 20 min at 75 °C to ensure the completeness of the derivatization reaction. Lowe et al. (27) reported a precision corresponding to an RSD of $\approx 1\%$ for 20-ng/mL solutions of formaldehyde in aqueous acidic DNPH. Furthermore, determination of formaldehyde in ambient air samples with the rotating-flask sampler developed by Lowe et al. gave values within 20% of those observed by a differential optical absorption technique (27) (see Section V.D.1.c [2]).

The accuracy and precision of methods involving tube sampling have also been found to be respectable. Although Fung and Grosjean (26) did not report the accuracy of determinations with their tube-sampling approach involving glass beads impregnated with DNPH, phosphoric acid, and poly(ethylene glycol), precision has been observed to be good with an RSD of 2.9% for formaldehyde levels in the range of 2.4 to 7.9 ppb. Beasley et al. (11) have validated their DNPH hydrochloric acid-coated silica gel in the concentration range of 100 to 3800 ppb. They obtained an average recovery of 94% with an RSD of 4% for 20-L air samples. Kuwata et al. (13) reported a limited validation of their DNPH sulfuric acid-coated Sep-Pak C₁₈ cartridge. Recoveries of 6- μ g spikes averaged 102% with an RSD of 4.2%. A 6- μ g spike corresponds to approximately 50 ppb in a 100-L spike. The precision of formaldehyde determination in a synthetic air sample corresponded to an RSD of 5.5% at an average observed level of 914 ppb. However, recoveries were not stated. In additional work, Kuwata et al. (13) reported that the precision of formaldehyde determinations in ambient air correspond to an RSD of 7.5% at average observed levels of 1.5 to 1.6 ppb. However, simultaneous determinations were not made by an independent method. Finally, Lipari and Swarin (5) recently completed a field validation of their Thermosorb/F cartridge containing DNPH-coated Florisil. The accuracy of the sampling method was determined relative to DNPH impinger sampling. In 60-L air samples, the average ratio of the cartridge results to impinger results was 1.02 for 10 samples taken at formaldehyde concentrations in ambient air ranging from about 1 to 6 ppb. Similar agreement was also found for measurements in foundry workplace air and automobile exhausts at concentrations between about 150 to 1200 ppb.

Storability/Stability. Once the dinitrophenylhydrazone of formaldehyde is formed, it can be stored prior to analysis if the proper precautions are

taken. Lowe et al. (27) have stored the product in excess DNPH solutions for up to two weeks in sealed Pyrex glass bottles at 4 °C. These investigators observed that the glass containers for the solutions have to be rinsed with dilute acid and DNPH solution prior to storage. Other authors have recommended that DNPH solutions should be stored at refrigerator temperatures after sampling (1,10,28,66). However, when desorbed into acetonitrile the derivative is reasonably stable. With the silica gel removed after the first day, sample solutions have been observed to be stable up to 20 days. Lipari and Swarin have demonstrated much better stability of the formaldehyde derivative on their sorbent tube containing Florisil impregnated with DNPH. Quantities of the derivative corresponding to 4.5 µg of formaldehyde have been found stable for at least three weeks at 21 °C when sealed in the tubes. These tubes were each spiked with 1000 L of ambient air containing formaldehyde at a concentration of 38 ppb.

(2) GC/helium ionization detection

Andrewes (32) reported the determination of formaldehyde in air by gas chromatography with helium-ionization detection (HID). Air is sampled with a 230-µL gas sample loop and injected onto a Porapak T column. The HID provides a sensitive but nonspecific detector for volatile compounds. Consequently, the sensitivity of the GC/HID for formaldehyde is limited to somewhat less than 800 ppb by the elution of the peak attributed to air near the formaldehyde peak. Water vapor does not interfere with formaldehyde because the Porapak T column allows the elution of formaldehyde about 4 min prior to the elution of the water peak. However, the large response to water vapor in ambient air limits the number of samples that can be analyzed in a given analysis period. The water peak may require as long as 40 min to elute. With laboratory test atmospheres, the method has demonstrated 92% recovery at the 800-ppb level with the CA approach as the reference method. Furthermore, Andrewes reported that precision corresponds to an RSD of 8.6% at the 800-ppb level.

The method in its present form does not seem entirely satisfactory for determining ambient levels of formaldehyde. However, several improvements are feasible that could make the technique a valuable and useful tool and that would be simple to use in ambient-air monitoring. One improvement that could easily be implemented is the proper selection and optimization of chromatographic conditions including the evaluation of other GC column packings that would better separate the air and formaldehyde peaks. A secondary improvement would be the use of a column backflush valve to reverse GC carrier-gas flow after the elution of the formaldehyde peak. Water could be backflushed out of the column before reaching the detector. A third improvement would be the operation of the HID in the pulsed mode to improve sensitivity. In fact, Brazell and Todd (56) have coupled a pulse generator to an HID and have found significant reductions in noise and background levels. Furthermore, the device can be operated at much higher voltages than a nonpulsed detector. Because HID response increases exponentially with increases in voltage, greater sensitivity for formaldehyde is likely with the pulsed detector. Brazell and Todd are currently empirically determining the sensitivity for individual compounds.

(3) Molecular sieve 13X - GC/MS

Yokouchi et al. (33) have developed a method involving the collection of formaldehyde on 13X molecular sieve with subsequent thermal desorption onto a gas chromatograph coupled with a mass spectrometer (GC/MS) (33). The advantages of this method include excellent sensitivity and selectivity. The pre-concentration of formaldehyde on molecular sieve 13X with subsequent thermal desorption of the entire sample onto the GC affords a detection limit of 0.3 ppb in a 1-L air sample. Interference by water is avoided by separation from formaldehyde on a Porapak T column. The formaldehyde is determined by MS with mass fragmentograms of the m/e 29 and 30 ions. Recovery studies with spiked tubes yielded 101% recovery of 1-ng and 10-ng quantities, corresponding to 0.8 and 8 ppb in 1-L air samples. Precision at these levels corresponds to an RSD of 14% for 1-ng spikes and 2% for 10-ng spikes. Another advantage is that formaldehyde is stable on the molecular sieve 13X for at least 24 h at ambient temperatures.

(4) Derivatization methods with determination by GC

Two derivatization methods involving determinations by GC have been published recently for formaldehyde (24,25). Neither of these methods has been found to offer the sensitivity necessary for the determination of formaldehyde at low parts-per-billion levels in air. However, both methods may possess considerable promise in being optimized to determine formaldehyde in ambient air.

One method as reported by Levine et al. (24) involves the reaction of benzyloxyamine hydrochloride with formaldehyde in buffered methanol solution to form formal-O-benzyloxime. The oxime is then determined by GC with thermionic detection, usually referred to as nitrogen-phosphorus specific detection (NPD). The use of the NPD avoids many interferences from atmospheric contaminants that do not contain nitrogen or phosphorus. Fortunately, the GC/NPD method is not sensitive to excess benzyloxyamine. Levine et al. reported that it is feasible to trap formaldehyde in impingers containing a solution of benzyloxyamine hydrochloride in methanol buffered with sodium acetate. They report efficiencies of 90% at 25 °C for conversion of the formaldehyde to its derivative; however, collection efficiencies of actual test atmospheres have not been performed. Nevertheless, they found that unspecified amounts of formal-O-benzyl-oxime were completely retained in impingers at 25 °C at an airflow rate of 0.75 L/min for 23.3 min or 17.5 L.

The detection limit is not reported by Levine et al. (24). But they do claim that aldehyde impurities in the methanol solvent set the experimental detection limit for C₁ to C₄ aldehydes. By analogy to the GC/NPD response for a methyl-O-oxime derivative, a detection limit of about 40 ppb is estimated. The detection limit for formaldehyde may actually be considerably lower. However, until the breakthrough volume is empirically determined and until the instrumental detection limit for the formaldehyde derivative is found, the detection limit for the overall sampling and analytical method cannot be defined.

Kennedy and Hill (25) reported a second derivatization approach that involves the reaction of formaldehyde with N-benzylethanolamine coated on Chro-

mosorb 102 to form 3-benzyloxazolidine. The coated Chromosorb 102 is packed into glass tubes for sampling. The oxazolidine derivative is desorbed with isooctane and determined by capillary GC with flame-ionization detection (GC/FID). With a 25-m by 0.2-mm-ID Carbowax 20-M fused-silica capillary column, the derivatives of formaldehyde, acetaldehyde, propionaldehyde, and *n*-butyraldehyde are separable. The investigators reported the limit of detection to be 1 µg/mL in a 2-mL isooctane extract. This corresponds to ≈270 ppb in a 12-L air sample. As with the other derivatization methods discussed, the factor limiting sensitivity appears to be contamination of the reagents with formaldehyde.

The breakthrough volume of a 120-mg bed of the coated Chromosorb 102 has been found to be about 16 L in test atmospheres at 80% RH and containing 8 ppm of formaldehyde and 6 ppm of acetaldehyde. Thus the 120-mg sorbent bed has a capacity for at least 160 µg of formaldehyde. Kennedy and Hill actually recommended that a 12-L air sample be taken for analysis. Because formaldehyde is collected on the tube by reaction, it is conceivable that the capacity of the tube is not strongly dependent on the air volume sampled. Consequently, the breakthrough volume for ambient levels of formaldehyde may, in fact, be higher than 16 L and high enough to allow accurate determinations with this method at concentrations much lower than 270 ppb.

The benzylethanolamine method has been validated in the concentration range of 400 to 3800 ppb with standardized test atmospheres. Kennedy and Hill reported that recoveries averaged 94.5% with a pooled precision corresponding to a RSD of 6.1%. The formaldehyde derivative is also stable on the sorbent tube. The investigators reported that the recovery of 37.6-µg spikes was 95.8% after storage for 7 days at room temperature.

c. Established techniques for continuous monitoring of formaldehyde

At least three instrumental analytical techniques have been developed that are capable of determining formaldehyde at ambient-air levels and that may be adapted to source monitoring. One of these is the automated pararosaniline method (18) discussed in detail in Section V.A.1.a.[3]. The portable CEA Continuous Colorimetric Analyzer has been used to apply the pararosaniline method with a limit of detection of 2 ppb. Two other instrumental techniques that have been found useful are long-path, Fourier-transform infrared (FTIR) spectroscopy (35,36), and differential UV-optical absorption spectroscopy (4). These are described in detail below.

(1) FTIR

The development of FTIR spectroscopy has extended infrared measurements to concentrations of air contaminants about 100 times lower than previously possible (35, 36). Consequently, the detection limit for formaldehyde determinations is now ≤5 ppb. This sensitivity is possible because of several innovative developments in optical science over the past 20 years. Folded path cells now allow path lengths as long as 1000 m in a cell housing that is only 20 to 23 m in length. Improvements in detector technology have improved signal-to-noise ratios. The major improvement, however, is the replacement of dispersive

IR spectrophotometers with Michelson interferometers equipped with computers to perform Fourier transforms of the resulting interferograms. The use of the interferometer has increased "throughput" of incident energy and has allowed multiplexing (i.e., the simultaneous observation of multiple spectral resolution elements). Multiplexing has resulted in signal-to-noise ratio gains of 10 to in excess of 100 times those attainable with dispersive IR spectrometers and, also, has resulted in high spectral resolution. In addition, digitized reference spectra have helped to overcome interferences. Ratios of sample spectra to reference spectra of known interferents have been used to enhance the absorption bands of formaldehyde.

Although the FTIR instrument is considered to be a reliable tool for obtaining formaldehyde concentrations, little information concerning the validity of such determinations is available. Hanst et al. (35) have estimated IR molar absorptivities for a number of air contaminants including formaldehyde, but the reliability of these estimations is unknown. Tuazon et al. (36) have obtained reference spectra with known quantities of formaldehyde released into the sample cell, but potential wall losses and the possibility of other sources of error are not dealt with. Grosjean and Kok (12) reported that they sampled standardized test atmospheres and compared the concentrations found by FTIR to concentrations found by the DNPH/HPLC and the CA methods. (Presumably Grosjean and Kok used the absorptivities reported by Hanst et al. in calibrating the FTIR.) For nominal formaldehyde concentrations of 30 to 380 ppb, they reported that the linear regression of DNPH/HPLC versus FTIR results yielded a slope of 0.95 and that CA results versus FTIR results yielded a slope of 0.89. However, they claimed that the comparison of FTIR to the other methods was not valid because sampling times were different. CA and DNPH/HPLC results were integrated over an hour while FTIR results were taken every few minutes.

Two primary disadvantages of long-path FTIR include the lack of portability of the system and the expense of the sophisticated equipment involved. The size of the gas sampling cell alone ($\approx 23 \times 0.81 \times 0.84$ m) limits the portability of the system. Consequently, air monitoring in remote locations or source monitoring does not seem entirely feasible unless the system could be mounted near the emission source. Nevertheless, at least one FTIR system has been mounted in a van for field studies (36). Furthermore, air samples have also been transported to FTIR systems in plastic bags (36).

(2) Long-path differential optical absorption spectroscopy

Platt et al. (4) reported the determination of formaldehyde in air by this technique. Three absorption bands in the near ultraviolet, 326.1, 329.7, and 339.0 nm, have been used for identification and quantification of formaldehyde. The light source, a Xenon high-pressure lamp, and the receiving mirror, a concave spherical mirror of 30-cm diameter and 1.8-m focal length, are separated by a distance of 5 to 10 km depending on atmospheric visibility. The light received is focused on the slit of a spectrometer. A rotating disk with radial slits located in the focal plane at the exit slit of the spectrometer scans 13-nm increments of the spectrum. The light passing through the radial slits is monitored by a photomultiplier. A microcomputer records and adds the superimposed intensities of scans for each 13-nm spectral solution. Thus, random

fluctuation of light intensity, atmospheric density, and current fluctuations are averaged out. The microcomputer also facilitates the subtraction of reference spectra from sample spectra to remove interference from ozone and nitrogen dioxide.

With this device, Platt et al. claimed a detection limit of 0.15 ppb for formaldehyde in air using a 5-km path length and a 20-min monitoring time. The instrument has been calibrated by determining the decadic differential absorption coefficient to be $20.4 \text{ (mole/L)}^{-1} \text{ cm}^{-1}$ at 326.1 nm. However, the authors did not report the accuracy of the overall method in relation to reference analytical methods. Lowe et al. (27) reported that the differential optical absorption technique indicated formaldehyde concentrations of 0.25 to 2.5 ppb that were within 20% of concentrations found by their DNPH/HPLC technique. As with the FTIR technique, the sophistication of the differential optical absorption technique limits its usefulness to only highly skilled technicians or scientists.

d. Exploratory techniques for continuous monitoring of formaldehyde

Several novel analytical techniques have been investigated for the determination of formaldehyde in air. Because these techniques have not been fully evaluated or because they presently are not entirely satisfactory, we discuss them as exploratory but promising methods.

(1) Chemiluminescent method

This method is based on the chemiluminescence (CL) produced by the reaction of gallic acid and hydrogen peroxide with formaldehyde in solution (6,12). The combined intensities of the major emissions bands at 643, 702 and 762 nm is proportional to the concentration of formaldehyde in the solutions. Grosjean and Kok (12) reported that formaldehyde in air is first collected in an impinger containing water. An aliquot of the solution is then analyzed by CL. For an air-sample volume of 60 L, the limit of detection corresponds to 0.6 ppb. When compared to three other air-sampling and analysis methods in laboratory tests at 30 to 320 ppb, the correlation of results by the CL approach to corresponding theoretical results by the FTIR and CA methods gave slopes that were 30 to 35% higher than unity. Although the slope of the linear regression curve comparing the CL results with the DNPH/HPLC results was 0.98, the correlation coefficient was disappointingly low (0.76). Furthermore, ambient-air determinations under heavy smog conditions revealed a large negative interference with the CL method. Results by the CL approach were about one third the results obtained by the CA and DNPH/HPLC method.

(2) Microwave spectrometric methods

Kamens and Jeffries (31) reported that Lawrence Livermore Laboratories (LLL) has developed a microwave spectrometer for the determination of formaldehyde in air. Ambient formaldehyde is enriched by selective permeation through a dimethyl silicone membrane to yield a limit of detection of 30 ppb. Hrubesh et al. (37) of LLL reported no interference from acetaldehyde, methanol, toluene, ammonia, or ethanol. However, a major limitation of the instrument is

its slow response to concentration fluctuations. Hrubesh et al. suggested that a major redesign of the instrument to include the heating of the inlet and microwave cavity would shorten response times.

(3) Laser-induced fluorescence methods

Kamens and Jeffries (31) reviewed a fluorescence technique originally described by Becker et al. (57) in 1975. Formaldehyde is excited by a frequency-doubled tunable dye laser in the wavelength range of 320 to 345 nm. Becker reported that concentrations as low as 40 ppb can be detected.

More recently, Mohlmann (58) reported an improved technique with a detection limit ($S/N = 3$) of 10 ppb of formaldehyde in dry air at a measuring time of 100 s. He uses a Q-switched Nd:YAG laser with frequency-tripled output at a wavelength of 354.7 nm. The intensity of the nondispersed fluorescence is measured using a color/interference filter (420 ± 5 nm) and a photomultiplier. The fluorescence spectrum has also been recorded with a monochromator-photomultiplier combination in the range of 360 to about 525 nm. Neither water vapor nor acetone has been found to quench the formaldehyde fluorescence. However, water vapor produces a significant background response that can be corrected if the relative humidity of the air sample is known.

(4) Photoacoustic laser spectrometric method

Currently, Atkinson (38) is adapting photoacoustic spectroscopy to the determination of aldehydes in air. His technique involves pulsed laser excitation of the analyte in the ultraviolet region (308 nm) in an evacuated chamber. A microphone responds to the time-dependent variations of pressure caused by the absorption of energy by the analyte. The photoacoustic waveforms are digitally stored and averaged to obtain a composite signal with random noise minimized. In preliminary work, Atkinson has demonstrated quantitative determinations of formaldehyde down to 3 ppm. However, he has suggested a number of improvements that could improve sensitivity. One improvement would be to substitute a tunable laser for the fixed-frequency laser. The 309-nm excitation energy causes significant photodecomposition of formaldehyde. A tunable laser should allow the selection of an excitation energy that is below the photodissociation threshold. Another improvement would be a better design of the sample cell to decrease background noise. Cells that provided greater isolation of the microphone and cell windows and less absorption of energy by the windows are currently being tested. Microphones of higher quality are also being used in current experiments.

2. Acetaldehyde

Methods that have been used to determine acetaldehyde in ambient air include the DNPH/HPLC method, the MBTH method, several GC methods, and some continuous monitoring techniques.

a. DNPH/HPLC method for acetaldehyde

The advantages of this method in the determination of acetaldehyde in air closely parallel those of the same approach applied to the determination of

formaldehyde (see Section V.D.1.b[1]). That is to say, that the approach has been found to be selective, sensitive, accurate, and precise. Variations of the method and their relative merits are discussed below.

DNPH Impinger Collection. Theoretically, the DNPH/HPLC method is applicable to the determination of any carbonyl compound in air providing an efficient collection medium is used. Most of the DNPH methods have been used to sample acetaldehyde as well as formaldehyde. Menzies, et al. (10) reported in a limited number of tests that they were able to collect acetaldehyde with an efficiency of $\approx 90\%$ in 60 L of diesel exhaust with 0.25% DNPH in 2 N HCl. However, Grosjean et al. (1,12,26,55) have shown that a hydrocarbon phase must also be present in the impinger solution to trap acetaldehyde efficiently in ambient air sampling. These authors have used n-hexane, cyclohexane, or isooctane. They report that the recovery of acetaldehyde from 6-L air samples rose from ≈ 20 to $\approx 100\%$ when hexane was added to the aqueous collection medium. Riggan (28,66) suggested the use of isooctane as the hydrocarbon phase in a DNPH/HPLC method written for the EPA for ambient air or source sampling. However, he does not present collection efficiencies. Singh et al. (29) reported that they sampled acetaldehyde in acidified DNPH in acetonitrile. But they did not report collection efficiencies. Tanner and Meng (7) reported a collection efficiency of 74% in 30-L air sample with an acidified DNPH acetonitrile solution.

DNPH Solid-Sorbent Collection. Several DNPH solid sorbent samplers have been evaluated as collectors of acetaldehyde. These have already been described in detail in Section V.D.1.b[1] as collection media for formaldehyde. Grosjean et al. (55) reported that their solid sorbent, which comprises glass beads coated with DNPH, polyethylene glycol, and phosphoric acid, collected acetaldehyde efficiently in dry air but not in humid air. Even in dry air, however, the breakthrough volume was less than 6 L at 200 ppb of acetaldehyde in air.

Kuwata et al. (12) reported the same excellent collection efficiency for acetaldehyde as reported for formaldehyde with their Sep-Pak C₁₈ cartridge impregnated with DNPH and phosphoric acid. Although Lipari and Swarin (5) did not determine the efficiency of their DNPH/Florisil sorbent for the collection of acetaldehyde, they did determine acetaldehyde in actual field tests. Water has not been found to affect the collection efficiencies of the Sep-Pak or Florisil sampler.

Interferences. As in the determination of formaldehyde, the determination of acetaldehyde by the DNPH/HPLC method is essentially interference free. As discussed in Section V.D.1.b[1], the following air contaminants do not interfere at typical concentrations: ozone, nitrogen dioxide, sulfur dioxide, peroxyacetylnitrates, free radicals, and other aldehydes.

Sensitivity. Limits of detection for acetaldehyde by DNPH/HPLC methods, whether impinger or sorbent sampling has been used, are comparable to those reported for formaldehyde above (see Section V.A.2.a). These limits are <1 to <3 ppb in 30- to 100-L air samples. As with formaldehyde also, contaminants in the DNPH, other reagents, and solvents have prevented the attainment of lower limits.

Accuracy and Precision. The accuracy and precision obtained with the DNPH/HPLC approach in the determination of acetaldehyde are comparable to the accuracy and precision obtained in the determination of formaldehyde by the same method. Grosjean and co-workers (1,12,26,55) recovered an average of 98% of spikes into impinger solutions for 6- to 113-ng quantities of acetaldehyde with RSDs of 1.1 to 1.9%. The overall method including air sampling, sample preparation, and HPLC analysis gave results that were within about 20% of the theoretical values in test atmospheres of 150 to 400 ppb of acetaldehyde in air. Tanner and Meng (7) reported linear calibration curves in the range of 10 to 75 ppb of acetaldehyde in standardized test atmospheres.

The accuracy and precision of at least one DNPH/HPLC approach involving sorbent sampling appears also to be favorable. Kuwata et al. (13) reported an average recovery of 96.5% with an RSD of 2.4% for 6- μ g spikes on DNPH/sulfuric acid-coated Sep-PAK C₁₈ cartridges. The precision of determinations of acetaldehyde in synthetic air samples yielded an RSD of 3.5% at concentrations near 500 ppb and RSDs of 7.2 to 8.7% for determinations at 3-ppb concentrations in ambient air. Apparently, no independent reference sampling-and-analysis method was used to assess accuracy in this laboratory or field testing.

Storage/Stability. The hydrazone derivative of acetaldehyde is stable in impinger solutions after the compound is formed. Grosjean (1) reported that impingers each containing 10 mL of acidic aqueous DNPH reagent and 10 mL of a 9:1 by volume mixture of cyclohexane and isooctane were spiked with 1.23 μ g of the hydrazone and then exposed to ambient air. After sampling 45 L of air containing 70 to 120 ppb of nitrogen dioxide, 65 to 170 ppb of ozone, and undetermined concentrations of sulfur dioxide, peroxyaclynitrates, free radicals, and other pollutants, the average recovery was found to be $100 \pm 10\%$ when compared to unspiked impingers. The stability of the hydrazone on reactive solid sorbents has not been reported.

b. MBTH method for acetaldehyde

The MBTH impinger-sampling and colorimetric-analysis method described above in Section V.D.1.a[4] can be used for the determination of acetaldehyde in air. However, several disadvantages of the method limit its usefulness for ambient air sampling or source sampling. The method is only quantitative for acetaldehyde when it has been calibrated with acetaldehyde standards and when no other aldehydes are present at significant concentrations. Thus, specificity and accuracy are questionable in actual ambient air testing. The Inter-society Committee on Methods of Air Sampling and Analysis (19) reported that the MBTH method was less sensitive to acetaldehyde and higher aldehydes than to formaldehyde. Reliable determinations of acetaldehyde can be done at concentrations in impinger solutions of no less than about 0.3 μ g/mL, or 3 μ g in a sample. This corresponds to only 70 ppb in a 25-L air sample (50 min at 0.5 L/min). However, the limit of detection can be extended by sampling a greater volume of air. Thus, a reliable determination could possibly be made at 2 ppb in 720-L air samples (24 h at 0.5 L/min).

c. Gas-chromatographic methods for acetaldehyde

(1) Impinger--GC/FID

One tentative method published by the Intersociety Committee involved the determination of aliphatic C₂ to C₅ aldehydes by a GC method (59). The aldehydes are collected in 1% sodium bisulfite solution. An aliquot of the solution is then injected into a glass GC inlet packed with sodium carbonate. The acetaldehyde-bisulfite adduct decomposes upon contact with the carbonate, and the free aldehyde is introduced onto the GC column. The limit of detection for a 120-L air sample is reported to be 20 ppb of acetaldehyde in air. No interferences are reported. No accuracy and precision data are available for atmospheric samples. However, it is reported that known standards in bisulfite solution can be determined to within 5% of their "true" value. When stored at 6 °C, sample solutions are stable for up to two days prior to analysis. Collection efficiencies are not reported. However, the breakthrough volume is apparently greater than the recommended air-sampling volume of 120 L if the impingers are immersed in an ice bath during sampling.

(2) Sorbent/cold trap--GC/FID

Bellar and Sigsby (31,60) reported a method that involved the concentration of acetaldehyde in a dry-ice cold trap. Air is first drawn through a GC column packing to collect acetaldehyde. The compound is then backflushed from the packing with carrier gas and trapped in a cold finger in a dry-ice bath. Subsequently, the temperature of the finger is raised and the acetaldehyde is flushed into the GC. The limit of detection for C₂ to C₅ aliphatic aldehydes is 30 to 80 ppb. Perhaps the limit of detection could be lowered by maximizing sampling volume. However, breakthrough volume is not discussed. Neither accuracy, precision, nor stability on the column packing are discussed.

(3) Sorbent/cold trap--GC/MS

In a survey of ambient air pollutants near industrial facilities and chemical waste dumps, Pellizzari (15) reported that acetaldehyde concentrations ranging from about 2 to 29 ppb are in 100- to 150-L air samples. His method involves the concentration of air contaminants on a 1.5 x 6.0 cm bed of the solid sorbent Tenax-GC (35/60-mesh) in a glass cartridge. The sorbed contaminants are thermally desorbed into a capillary cold trap and then thermally transferred to a GC capillary column and detected by mass spectrometry. Because the technique has not been specifically evaluated for the determination of acetaldehyde, the accuracy and precision of the determinations and the storability of acetaldehyde on Tenax-GC are unknown. A great advantage of the method is the high specificity of mass-spectrometric detection. Thus, the method allows the identification of acetaldehyde in polluted ambient air.

(4) Direct injection--GC/FID

Kamens and Jeffries (31) reported a GC method that involved conversion of aldehydes to methane to increase sensitivity. Two-milliliter air samples are directly injected onto a Porapak Q column. After elution of light hydrocarbons, the eluting aldehydes including acetaldehyde are chemically reduced to

hydrocarbon gases. Subsequently, the hydrocarbons are detected by an FID. The limit of detection is reported to be 10 ppb of acetaldehyde in air.

(5) Derivatization--GC/NPD

Levine et al. (24) described the collection and derivatization of acetaldehyde in air by benzyloxyamine hydrochloride in methanol solution with a sodium acetate buffer. Air was sampled into impingers containing the solution. The resulting O-benzyl oxime of acetaldehyde was then determined by GC/NPD. The NPD allowed a high degree of selectivity because of its poor response to compounds that do not contain nitrogen or phosphorus atoms. The application of this procedure to the determination of formaldehyde is discussed in Section V.D.1.b[4] along with many details of the technique that will not be repeated here. Levine and co-workers reported an efficiency of 97% at 25 °C for the conversion of acetaldehyde to its derivative; however, collection efficiencies in impinger solutions are not reported. Thermionic detection (NPD) affords picogram sensitivity; however, the investigators report that aldehyde impurities in the methanol solvent set the experimental detector limit. No limit is stated for acetaldehyde. But it is estimated that concentrations on the order of 40 ppb could be determined by analogy to the determination of the nonanal derivative of methyloxyamine. During the development of this method, GC/MS was used to verify the identity of the derivatives.

d. Promising techniques for the continuous monitoring of acetaldehyde

There appear to be no well established and validated continuous monitoring methods for the determination of acetaldehyde at ambient air levels. FTIR can probably be applied to the determination of low-ppb levels of acetaldehyde. But apparently this application has not been documented in the current literatures. A microwave spectrometer has been designed to detect acetaldehyde and several other air contaminants of industrial hygiene significance (31,37). However, the detection limit for acetaldehyde is 16 ppm, about 10,000 times higher than required for ambient air monitoring. The same photoacoustic laser spectrometric technique described in Section V.A.4.d for the determination of formaldehyde has also shown considerable promise for determining acetaldehyde (38). In fact, Atkinson demonstrated quantitative determinations down to 100 ppb of acetaldehyde in air. Furthermore, he expects to be able to improve detectability by using a tunable laser for excitation, by altering the design of the sample cell, and by using more state-of-the-art microphones.

3. Acrolein

Several sampling and analysis approaches have been applied to the determination of acrolein in air. However, few have been evaluated thoroughly. The subsequent paragraphs discuss the information available with respect to currently used methods.

a. 4-Hexylresorcinol method for acrolein

In a 1965 publication, the Interbranch Chemical Advisory Committee of the U.S. Public Health Service recommended the 4-hexylresorcinol method over others

for acrolein because of its greater sensitivity and specificity (61). This method was originally developed by Cohen and Altschuller (16). In 1977, the method was published by the Intersociety Committee of the American Public Health Association as Method 114 (21) with only a few changes from the original version. As a portion of another method (APHA Method 116) originally devised by Lenagge et al. (42) for C_1 - C_5 aldehydes, the 4-hexylresorcinol is applied to an aliquot of a 1% sodium bisulfite collection medium. The method is based on the reaction of acrolein with 4-hexylresorcinol in a solution of trichloroacetic acid and mercuric chloride in ethanol. The trichloroacetic acid is actually added to the ethanol as a saturated solution in water. The product of the reaction is blue with a strong absorbance maximum at 605 nm. Impinger sampling with the mixed reagent has a collection efficiency of 95% for two impingers in series for 60-L air samples taken at 1 to 2 L/min.

The method is free of interferences from ordinary concentrations of sulfur dioxide, nitrogen dioxide, ozone, and most organic air contaminants. A small but insignificant interference is caused by olefins. Other aldehydes form a red product with the reagents. However, this product does not interfere with the determination of acrolein.

No accuracy and precision data are reported for the method. An estimate of the detection limit is 10 ppb in a 50-L air sample based on a difference of 0.05 absorbance unit from the blank using a 1-cm cell.

Once exposed to acrolein, the sampling solution is stable for only about 3 h. If the acrolein is collected in ethanol or sodium bisulfite in water, the resulting solutions can be stored several days if the solutions are refrigerated. Subsequent to storage, 4-hexylresorcinol and trichloroacetic acid, are added to an aliquot of a solution for color development.

b. DNPH/HPLC method for acrolein

Acrolein is among the several volatile aldehydes that have been determined by the DNPH/HPLC approach. Lipari et al. (62) used the method to determine acrolein in the effluent from burning wood. Riggin (28,66) has recommended DNPH/HPLC method with impinger sampling as a reliable technique for determining acrolein in ambient air and source sampling. However, neither Riggin nor Lipari et al. have assessed the validity of the method in determining acrolein.

At least one DNPH/HPLC method involving sorbent-tube sampling has also been used to determine acrolein in air. Kuwata et al. (13) performed field tests of their DNPH/hydrochloric acid-coated Sep-PAK cartridges as a sampler for C_1 to C_4 aldehydes and detected acrolein at levels around 0.3 ppb in municipal incinerator emissions. However, the accuracy and precision of these ambient air determinations were not assessed. No interferences were reported. The stability of the hydrazone resulting from reaction of DNPH with acrolein was not determined.

c. GC methods for acrolein

Numerous GC methods have been developed for the determination of acrolein. Several have involved the direct determination of acrolein after collection of

solid sorbents such as Tenax GC (15), 13X molecular sieves, hydroquinone-treated charcoal (64), and various porous polymers in tandem with activated charcoal (34). One method involves the derivatization of acrolein on a solid sorbent (65). Another method proposes the collection of acrolein in glass bulbs or plastic bags but gives little information to support the validity of the approach (30).

Hurley and Ketcham (64) have developed an industrial hygiene air-sampling-and-analysis approach involving the collection of acrolein on hydroquinone-treated charcoal. The sorbent acrolein is extracted from the treated charcoal with 1,2-dichloroethane, and the extract is then analyzed for acrolein by GC/FID. The sensitivity of the method is adequate for the determination of acrolein in workplace air but only marginally acceptable for ambient air and source monitoring. The limit of detection is estimated to correspond to 20 ppb in 5-L air samples. The empirically determined breakthrough volume is about 6 to 7 L of air for 100 mg of treated charcoal and is not significantly affected by the relative humidity of the air sample. In accuracy and precision tests with standardized test atmospheres, the recovery ranged from 69 to 76% at 50 ppb of acrolein in air. Precision corresponded to RSDs of 1 to 2% for determinations at concentrations of 50 to 60 ppb. Acrolein sorbed on the tubes is not stable for more than a day at room temperature. However, sorbed acrolein is stable for at least five days when exposed tubes are stored at -22 °C. The specificity of the GC analysis procedure avoids interference from a variety of air contaminants, including propylene, acrylic acid, acetaldehyde, acetic acid, isopropyl ether, and acetone.

Among the other solid sorbents that have been used to collect acrolein, Tenax-GC and 13X molecular sieves have shown considerable promise. Pellizzari (15) found 0.3- to 1.8-ppb levels of acrolein downwind from a waste disposal site. His method involved the sampling of 100-L air volumes through a Tenax-GC cartridge. The sorbed species were then thermally desorbed into a cold trap and subsequently vaporized and determined by GC/MS. The reliability of the techniques was not determined for acrolein. Nevertheless, determination by GC/MS allowed excellent specificity in identifying the compound as an air contaminant in the presence of a multitude of other contaminants. Gold et al. (63) reported 13X molecular sieves to be an efficient collector of acrolein in air. Water vapor was found to be deleterious to the capacity of the sorbent for acrolein. However, even at 100% RH, an air sample volume of 8 L/g of sorbent was allowed. The recovery of 3- to 8- μ g spikes of acrolein extracted from 1 g of 13X molecular sieves with distilled water was $90 \pm 11\%$. The recovery of 60 to 200 μ g spikes was $90 \pm 7\%$. Sorbed acrolein was found to be stable for over four weeks when stored at 0 °C. One major disadvantage of the method is its limited sensitivity. Gold et al. reported that 110 ppb of acrolein can be detected in an 8-L air-sample volume.

West et al. (34) described a four-stage solid-sorbent sampler that was evaluated for the collection of air contaminants, including acrolein, for subsequent thermal desorption and determination by GC/MS. Several grams of each of Tenax-GC, Porapak R, and Amborsorb 340 were packed into individual tubes. The tubes were then attached in tandem in the following order: Tenax-GC, Porapak R, and Amborsorb 340. Also, a second Amborsorb 340 tube was attached as a back-up to the first Amborsorb tube. In laboratory testing with test

atmospheres of mixed contaminants, recoveries of unspecified quantities of acrolein from all three types of sorbents were low when compared to theoretical concentrations in the test atmospheres. However, it is uncertain whether or not the low recoveries were the result of low desorption efficiencies or of the poor generation of test atmospheres. In actual field tests in Houston, acrolein was tentatively identified on the Tenax-GC portion of the sampler but the concentration was not reported.

Kennedy et al. (25) developed a GC method that involved the derivatization of acrolein with oxazolidine. Acrolein in air reacts with 10% (w/w) 2-(hydroxymethyl) piperidine coated on Amberlite XAD-2 to produce a bicyclic oxazolidine. The derivative was desorbed from the sorbent material with toluene, and the extract was analyzed by GC/NPD.

The accuracy and precision of the oxazolidine method were determined in the range of about 55 to 700 ppb. Average recoveries were 127% at 55 ppb, 97% at 150 ppb, and 100% at 700 ppb. The pooled RSD found over the range of the method was 11.1%. The acrolein derivative corresponding to a 2.6- μ g spike of acrolein sampled from standardized test atmospheres was stable for up to 28 days. No interferences were reported for the sampling-and-analysis method. The limit of detection of the method was also not reported. Consequently, the usefulness of the method for ambient-air sampling is uncertain.

4. Recommendations for the sampling and determination of aldehydes

A number of methods for the determination of formaldehyde have been demonstrated to be reliable for measurements in ambient air and in effluent from emission sources. These include the CA method, the pararosaniline method, and the DNPH/HPLC method with impinger and solid-sorbent sampling. For acetaldehyde, only the DNPH/HPLC method has been demonstrated to be reliable although the several GC techniques that have been applied to the determination of acetaldehyde appear promising. Only the colorimetric 4-hexylresorcinol method has been evaluated enough to demonstrate its present utility in determining acrolein in ambient air. However, even this method has not been rigorously validated. The DNPH/HPLC methods and the oxazolidine derivatization procedure also show considerable promise. But neither of these have been validated for the determination of acrolein.

The DNPH/HPLC method seems to show the greatest potential in providing a single method that can be used to determine the three aldehydes of interest and others. The DNPH solid-sorbent samplers especially offer simplicity and convenience in taking air samples. However, these samplers and the DNPH/HPLC analysis method itself require more extensive evaluation for acetaldehyde and especially acrolein determinations. EPA Method T05 was developed by Riggins (28,66) and has been used to determine 14 aldehydes and ketones in air samples. Low detection limits (≤ 1 ppb) and a freedom from interferences make this method particularly attractive. The use of impingers to take samples is the method's biggest disadvantage. After validation EPA Method T05 could be readily applied to ambient-air and source monitoring.

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TABLE 30. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF FORMALDEHYDE

Method No.	Principle	Potential Interferences	Limit of detection ^a	Accuracy and precision	Breakthrough volume	Storage stability	References
1. Chromotropic acid (CA) active sampling	Collection in water or 1% sodium bisulfite in impingers. Reaction with CA in presence of sulfuric acid. Spectrophotometric determination at 580 mμ.	Ethanol and higher alcohols, phenols, olefins, cyclohexanone, aromatic hydrocarbons.	100 ppb in 25 L of air. (122 μg/m ³)	Analysis: Agreement within 5% for three-laboratory survey, 1 to 20 μg. RSD 45%. Results comparable to Du Pont Pro-10k badge results. 98% collection efficiency with two impingers in tandem.	>440 L for one impinger. >120 L for two impingers in tandem.	After color development: 3% loss in 1 day, 10% in 8 days. Not discussed.	31,42, 43 9
2. Passive sampling	Diffusion into tube and fixation on glass-fiber filter impregnated with sodium bisulfite. Desorption with water. Determined as specified above.	Ethanol and higher alcohols, phenols, olefins, cyclohexanone, aromatic hydrocarbons.	6 ppb/week (7 μg/m ³) (theoretical), 18 ppb/week (practical) (22 μg/m ³).	+15% bias versus impinger sampling; RSD = 6.7%. Accuracy reduced when RH >60% at 25 °C.	Capacity >1000 ppm/h.	Sampler stable for >2 weeks, before or after exposure.	8,22
	Permeation through polydimethylsiloxane (PDMS) membrane into 1% sodium bisulfite solution. Determined as specified above. (Sampler marketed by Du Pont.)	Free of interferences from n-butanol, ethanol, toluene, and phenol.	10 ppb/week (12 μg/m ³), 40 ppb/24 h (48 μg/m ³).	11% of "true" result from 1,600 to 54,000 ppb/h; RSD = 5.5%. Must expose for >72 h to yield results comparable to impinger sampling at ppb levels.	Capacity not discussed.	Sampler stable for 2 weeks after exposure.	8,9
	Diffusion into badge. Collection on pad impregnated with sodium bisulfite. Determined as specified above. (Sampler marketed by 3M Company.)	Not discussed. Probably same as impinger method.	5 ppb/week, (6 μg/m ³)	42% of "true" result unless RH <40%. Results then are 70% low.	Capacity ≈72 ppm/h.	Sampler stable for 4 weeks after exposure.	8,46
3. Pararosaniline method	Active collection in water in impingers. Complexation with tetrachloromercurate and sulfite ion. Spectrophotometric determination at 570 mμ.	Slight interference from: Acetaldehyde-- 5 μg/mL yields 10% I; Propionaldehyde-- 50 μg/mL yields 10% I.	2 ppb in 30 L of air. (3 μg/m ³)	NA	NA	NA	12

(continued)

TABLE 30 (continued)

Method No.	Principle	Potential Interferences	Limit of detection ^a	Accuracy and precision	Breakthrough volume	Storage stability	References
3. Pararosaniline method (continued)	Same as above except reaction procedure modified by omitting tetrachloromercurate ion.	Sulfur dioxide: Interference minimized by addition of sodium hydroxide to sample solution. Cyanide ion: Interference minimized by addition of heavy metal ions.	25 ppb in 60 L of air. (31 µg/m ³)	Not statistically different from CA method at 95% confidence level when determining 50 ppb, RSD ≈20%.	>1 m ³	Exposed solutions stable for 2 weeks under refrigeration.	50
	Automated method of collection and analysis. Collected in solution of tetrachloromercurate ion and sulfite ion with subsequent color development and absorbance measurement automatically performed. (CEA Instruments.)	None reported but same as cited in Reference 18 above: Slight interference from acetaldehyde and propionaldehyde.	2 ppb (4.5 min lag time). (3 µg/m ³)	±3% agreement with CA method. Reproducibility was 1%.	NA	NA	18,52
	Active collection on 13X molecular sieves by active air sampling. Desorption with water. Determination by modified pararosaniline procedure (see Reference 50).	None reported but same as cited in Reference 50: Sulfur dioxide and cyanide ion.	25 ppb. (31 µg/m ³)	Close agreement with CA method in range of 25 to 100 ppb.	NA	NA	51
	Passive collection by permeation through PDMS membrane into water reservoir. Determination by modified pararosaniline procedure (see Reference 50).	None reported but same as cited in Reference 50: Sulfur dioxide and cyanide ion.	25 ppb. (31 µg/m ³)	±25% of "true" value.	NA	NA	51
4. 3-Methyl-2-benzothiazolone hydrochloride (MBTH) method	Active collection in aqueous 0.05% MBTH in impingers. Oxidation of resulting azine by ferric chloride/sulfamic acid aqueous solution to form blue cationic dye. Spectrophotometric determination at 628 nm.	Interferents include other aldehydes, imino heterocyclics, carbazoles, azo dyes, stilbenes, Schiff's bases, 2,4-dinitrophenyl hydrazones of aliphatic aldehydes, compounds containing p-hydroxylstyryl group, sulfur dioxide. Sulfur dioxide interference is eliminated by sulfamic acid.	10 ppb in 60 L of air. (12 µg/m ³) 30 ppb in 25 L of air. (36 µg/m ³)	Analysis: Agreement to within ±5% of "true" value Air sampling and analysis: Agreement to within ±10% of "true" value of 1 ppm in air.	720 L for one impinger with 84% efficiency. 99% efficiency with two impingers.	After exposure, prior to color development, 5% loss in 13 days at room temperature.	10,19

(continued)

TABLE 30 (continued)

Method No.	Principle	Potential Interferences	Limit of detection ^a	Accuracy and precision	Breakthrough volume	Storage stability	References
5. 6-Amino-1-naphthol-3-sulfonic acid (J-Acid)	Acid collection in impinger containing water. Solution reaction with J-acid. Spectrophotometric determination at 520 nm.	Other aldehydes including acrolein at high concentrations.	Analytical: 0.7 to 0.1 µg/mL.	NA	NA	NA	10, 20, 31
6. 2,4-Dinitrophenylhydrazine/high-performance liquid chromatography (DNPH/HPLC)	Active collection in impingers containing 0.25% DNPH in aqueous 2 N hydrochloric acid with or without a hydrocarbon solvent layer. Extraction into dichloromethane (DCM) or DCM and hydrocarbon solvent. Evaporation to dryness. Dissolution of residue in methanol or acetonitrile. Determination by HPLC with UV detection.	NA	1 to 10 ppb in 60 L of air. (1-12 µg/m ³)	Analysis: 96% recovery of 4- to 19-ng amounts with an RSD of 4.2%. Sampling and analysis: Agreement to within 25% when compared to CA and FIIR at 120 to 320 ppb.	>6 L for 100 ppb for one impinger with 90% efficiency. Moderate size high blanks. ambient >80 L with two impingers in ice bath.	Absorbing solution made up within 48 hr of sampling to minimize high blanks.	1,10, 12, 26, 28-30, 55,66
	Active collection in rotating glass drum packed with raschig rings, which are rotated into pool of DNPH/sulfuric acid absorbing solution. Determination by HPLC/UV.	NA	0.2 ppb in 2000 L of air. (0.3 µg/m ³)	Analysis: RSD of $\pm 1\%$ at 20 ng/mL. Sampling and analysis: Agreement to within 20% of low-ppb-levels determined by differential optical absorption spectroscopy.	>2000 L.	Product hydrazone stable in excess DNPH solution for >2 weeks when sealed in glass containers and stored at 4 °C.	27
	Active collection impingers containing DNPH and sulfuric acid in acetonitrile in ice bath. Exposed solution heated to 75 °C for 20 min. Determination by HPLC/UV.	NA	<1 ppb in 30 L of air. (<1 µg/m ³)	Analysis: Linear calibration curves in range of 50 to 150 ppb of formaldehyde in air. Sampling and analysis: Good correlation with CA method. Error estimated to be $\pm 10\%$ at low-ppb-level.	>30 L with 80% collection efficiency.	NA	7,29
	Active collection in sorbent comprising DNPH, phosphoric acid, and polyethylene glycol on glass beads. Extraction into DCM. Evaporation of solvent. Dissolution in acetonitrile. Determination of HPLC/UV.	NA	<3 ppb in 60 L of air. (<3 µg/m ³)	Analysis: 96% recovery of 4- to 19-ng amounts with an RSD of 4.2%. Sampling and analysis: Precision corresponding to an RSD of 2.9% for 2.4 to 7.9 ppb levels.	>6 L for 100 ppb at 50% Rf. (86% efficiency). >6 L in dry air.	NA	12,55

(continued)

TABLE 10 (continued)

Method	Principle	Potential Interferences	Limit of detection ^a	Accuracy and precision	Breakthrough volume	Storage stability	References
	Active collection on sorbent comprising silica gel coated with DNPH and hydrochloric acid. Desorption with acetonitrile, determination by HPLC/UV.	NA	80 ppb in 20 L of air. (98 µg/m ³)	Sampling and analysis: 94% recovery for 20-L air samples at 100 to 3800 ppb, RSD of 4%.	>20 L, 1300 mg of sorbent, 90% efficiency at 0.1 L/min. Capacity >100 µg.	>30% loss of derivative from tube in 5 days. Solution extracts stable for 9 days. With silica gel removed from extract, stable for 29 days.	11
	Active collection on sorbent comprising Sep-Pak C ₁₈ cartridge coated with DNPH and phosphoric acid. Desorption with acetonitrile, determination by HPLC/UV.	NA	<1 ppb in 100 L of air. (<1 µg/m ³)	Analysis: 102% recovery of 6-µg spikes with RSD of 4.2%. Sampling and analysis: RSD of 5.5% at 914 ppb, RSD of 7.5% at 1.5 to 1.6 ppb. No accuracy data available.	>100 L/1 mg of DNPH at <2 ppb (<9% efficiency), >10 L/1 mg of DNPH at 900 ppb (100% efficiency).	NA	13
	Active collection on sorbent comprising Florisil (thermosorb/f cartridge) coated with DNPH. Desorption with acetonitrile. Determination by HPLC/UV.	NA	<1 ppb in 100 L of air. (<1 µg/m ³)	102% recovery relative to DNPH impinger sampling at 1 to 6 ppb.	>100 L/1.2 g of sorbent at 92 ppb (>95% efficiency).	4.5 µg samples of formaldehyde stable on sorbent for >21 days at 21 °C.	5
7. Gas chromatography with helium ionization detection (GC/FID)	Active sampling of air with gas sampling loop. Sequential injection of sample into GC.	NA	<800 ppb in 230 µL of air. (<980 µg/m ³)	Sampling and analysis: 92% recovery at 800-ppb level, RSD = 8.6%.	NA	NA	32
8. Gas chromatography with mass spectrometric detection (13X molecular sieves--GC/MS)	Active collection on 13X molecular sieves. Thermal desorption and determination by GC/MS.	NA	0.3 ppb in 1 L of air. (<0.4 µg/m ³)	Analysis: 101% recovery of 1 ng with and RSD of 14%, 101% recovery of 10 ng with an RSD of 2%.	2 L/1 g of sorbent with a high RH, >3 L in dry air.	Sorbed formaldehyde is stable for >24 h at moderate ambient temperatures.	33
9. Gas chromatography with thermal ionization detection for nitrogen and phosphorus compounds (Benzylloxamine--GC/NPD)	Active collection in impingers containing benzylloxamine hydrochloride in methanol buffered with sodium acetate. Formaldehyde reacts to form formal-o-benzylloxime, which is then determined by GC/NPD.	NA	≈40 ppb. (48 µg/m ³)	Sampling and analysis: 90% conversion of formaldehyde to its derivative at 25 °C in 23 min.	Breakthrough of formaldehyde is not discussed.	Not discussed.	24

(continued)

TABLE 30 (continued)

Method No.	Principle	Potential Interferences	Limit of detection ^a	Accuracy and precision	Breakthrough volume	Storage stability	References
10. Gas chromatography with flame-ionization detection (N-benzylethanolamine--GC/FID)	Active collection on sorbent coating Chromosorb 102 coated with N-benzylethanolamine. Formaldehyde reacts to form 3-benzylloxazolidine, which is desorbed with isooctane and determined by capillary GC/FID.	NA	~270 ppb in 12 L of air. (331 µg/m ³)	Sampling and analysis: 94.3% recovery at 400 to 3000 ppb, RSD = 6.1%.	16 L/100 mg of sorbent at 80% RH and 8 ppm of formaldehyde.	37.6 µg of sorbed formaldehyde stable for 7 days at room temperature (95.8% recovery).	25
11. Fourier-transform infrared spectroscopy (FTIR)	Active sampling into a fixed gas cell, interferometric/spectroscopic determination in the infrared region at a wavelength of 3.62 µm.	NA	<5 ppb with 1000-m path length. (<6 µg/m ³)	Sampling and analysis: Linear regression of laboratory measurements suggests agreement to within 10% of CA results and to within 5% of DNPH/HPLC results for 30 to 300 ppb.	NA	NA	12, 35, 36
12. Long-path differential optical absorption spectroscopy	Differential spectrophotometric determination in the near ultraviolet region at three absorption bands, 326.1, 329.7, and 339.0 nm. The separation of a mobile light source and mobile receiving mirror determine the absorption path length.	Ozone and nitrogen dioxide interference minimized by the subtraction of reference spectra.	0.15 ppb with 5-km path length. (0.2 µg/m ³)	Sampling and analysis: Agreement to within 20% of DNPH/HPLC results for 0.25 to 2.5 ppb.	NA	NA	4, 27
13. Chemiluminescent (CL) method	Measurement of chemiluminescent radiation produced by reaction of gallic acid and hydrogen peroxide with formaldehyde in solution. Major emission bands are 643, 702, and 762 nm.	Undetermined constituents of heavy smog decrease response by about 30%.	0.6 ppb in 60 L of air. (0.7 µg/m ³)	Sampling and analysis: Poor correlation with DNPH/HPLC for 30 to 380 ppb. Linear regression of laboratory measurements suggest agreement to within 30 to 35% of CA and FTIR.	NA	NA	12
14. Microwave spectroscopy	Passive sampling by permeation through PDMS membrane. Spectrophotometric determination in the microwave region.	NA	30 ppb. (36 µg/m ³)	NA	NA	NA	31, 37
15. Laser-induced fluorescence spectroscopy	Active sampling into a fixed gas cell. Excitation of formaldehyde with a laser in the wavelength range of 320 to 355 nm. Measurement of nondispersed fluorescence near 420 nm.	Water vapor produces a significant background response that can be corrected if relative humidity is known.	10 to 40 ppb. (12-48 µg/m ³)	NA	NA	NA	31, 37, 38

(continued)

TABLE 10 (continued)

Method No.	Principle	Potential interferences	Limit of detection ^a	Accuracy and precision	Breakthrough volume	Storage stability	References
16. Photoacoustic laser spectroscopy	Air sample introduced into a sealed, evacuated gas cell. Excitation of formaldehyde with a pulsed laser at 308 nm. Measurement of pressure variations over time with a microphone.	Excitation energy (308 nm) causes significant decomposition of formaldehyde.	3 ppm. (4 µg/m ³)	NA	NA	NA	38

$$^a \text{Calculated from } \mu\text{g}/\text{m}^3 = \frac{P \cdot (MW) \cdot (ppb) \cdot 10^3}{(82.07) \cdot T}$$

where

P = pressure in atmospheres

MW = molecular weight
 $82.07 = \frac{\text{cm}^3 \cdot \text{atm}}{\text{deg. mole}}$

T = absolute temperature (°K)

TABLE 31. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF ACETALDEHYDE

Method No.	Principle	Limit of detection ^a	Analysis and precision	Breakthrough volume	References
1. 2,4-Dinitrophenyl hydrazine/high-performance liquid chromatography (DNPH/HPLC)	Active collection in impingers containing 0.25% DNPH in aqueous 2 N hydrochloric acid. Extraction into dichloromethane (DCM). Evaporation to dryness. Dissolution of residue in acetonitrile. Determination by HPLC with UV detection.	10 ppb in 60 L of air. (18 µg/m ³)	Sampling and analysis: Agreement to within ±10% of "true" value.	NA	10,
	Active collection in impingers containing 0.25% DNPH in aqueous 2 N hydrochloric acid with a hydrocarbon sorbent layer. Analysis as described above.	<1 to <3 ppb in 30 to 60 L of air.	Analysis: 98% recovery of 6- to 113-ng amounts of RSD of <2%. Sampling and analysis: Agreement efficiency to within 20% of "true" values.	>6 L for 100 ppb for one impinger with 10%. >30 L with a collection efficiency of 74%.	1,12,26, 28,30,55, 66
	Active collection in impingers containing DNPH and sulfuric acid in acetonitrile in ice bath. Exposed solution heated to 75 °C for 20 min. Determination in acetonitrile. Determination by HPLC/UV.	<1 ppb in 30 L of air. (<2 µg/m ³)	Analysis: Calibration curves were linear in the range of 10 to 75 ppb.		7,29
	Active collection on sorbent comprising DNPH, phosphoric acid, and polyethylene glycol on glass beads. Extraction into DCM. Evaporation of sorbent. Dissolution in acetonitrile. Determination by HPLC/UV.	<3 ppb in 60 L of air. (<5 µg/m ³)	Analysis: 98% recovery of 6- to 113-ng amounts with RSD of <2%. Sampling and analysis: Precision corresponded to RSD of 5.90% for 0.47 to 1.62 ppb.	~60 L for 10 ppb with 76% efficiency in dry air. <60 L at 50% RH.	12,55
	Active collection on sorbent comprising Sep-Pak C ₁₈ cartridge coated with DNPH and phosphoric acid. Desorption with acetonitrile. Determination by HPLC/UV.	<1 ppb in 100 L of air. (>2 µg/m ³)	Analysis: 96.5% recovery of 6-µg spikes with RSD of 3.5% at 500 ppb, RSDs of 7.2 to 8.7% at 3 ppb. No accuracy data given.	>100 L/1 ng of DNPH at <2 ppb. >10 L/1 ng of DNPH at 900 ppb.	13
	Active collection on sorbent comprising Florisil (Thiemborsorb/F cartridge) coated with DNPH. Desorption with acetonitrile. Determination by HPLC/UV.	1 ppb in 100 L of air. (2 µg/m ³)	NA	NA	10

(continued)

TABLE 31 (continued)

Method No.	Principle	Limit of detection ^a	Accuracy and precision	Breakthrough volume	References
2. MBTH (3-methyl-2-benzothiazolone hydrazone hydrochloride) method	Active collection in aqueous 0.05% MBTH in impingers. Oxidation of resulting azine by ferric chloride/sulfamic acid aqueous solution to form blue cationic dye. Spectrophotometric determination at 628 nm.	70 ppb in 25 L of air. (126 µg/m ³) 2 ppb in 720 L of air. (4 µg/m ³)	NA	NA	10,19
3. Impinger--GC/FID	Active collection in impingers in aqueous 1% sodium bisulfite solution in an ice bath. Injection of solution aliquot into GC inlet packed with sodium carbonate. Determination by GC/FID.	20 ppb in 120 L of air. (36 µg/m ³)	Analysis: Agreement to within 5% of "true" value.	>120 L	59
4. Sorbent/cold trap--GC/FID	Active collection on GC column. Acetaldehyde back-flushed into dry-ice cold trap. Trap heated to release acetaldehyde into GC column. Determination by GC/FID.	30 to 80 ppb. (54 to 144 µg/m ³)	NA	NA	31,60
5. Direct injection--GC/FID	Direct injection of 2-ml air samples onto Poropak Q column. Chemical reduction to ethane upon elution. Determination by FID.	10 ppb in 2 ml of air. (18 µg/m ³)	NA	NA	31
6. Derivatization--GC/NPD	Active collection in impingers containing benzyloxamine hydrochloride in methanol buffered with sodium acetate. Acetaldehyde reacts to form acetol- <u>O</u> -benzylloxime which is then determined by GC/NPD.	40 ppb. (72 µg/m ³)	Sampling and analysis: 9% conversion of acetaldehyde to its derivative at 25 °C in 23 min.	NA	24

(continued)

TABLE 31 (continued)

Method No.	Principle	Limit of detection ^a	Accuracy and precision	Breakthrough volume	References
7. Microwave spectroscopy	Passive sampling by permeation through polydimethylsiloxane (PDMS) membrane. Spectrophotometric determination in the microwave region.	16 ppb. (29 µg/m ³)	NA	NA	31
8. Photoacoustic laser spectroscopy	Air sample introduced into a sealed evacuated gas cell. Excitation of acetaldehyde with a pulsed laser at 308 nm. Measurement of pressure variations over time with a microphone.	100 ppb. (180 µg/m ³)	NA	NA	38

$$^a \text{Calculated from } \mu\text{g/m}^3 = \frac{P \cdot (HW) \cdot (\text{ppb}) \cdot 10^3}{(82.07) \cdot I}$$

where

p = pressure in atmospheres

HW = molecular weight

82.07 = gas constant in $\frac{\text{cm}^3 \cdot \text{atm}}{\text{deg. mole}}$

I = absolute temperature (°K)

TABLE 32. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF ACROLEIN

Method No.	Principle	Potential Interferences	Limit of detection ^a	Accuracy and precision	Breakthrough volume	Storage stability	References
1. 4-Hexylresorcinol method	Active collection of formaldehyde in impingers containing a solution of 4-hexylresorcinol, trichloroacetic acid, and mercuric chloride in ethanol. The product formed is blue with a strong absorbance maximum at 605 nm.	Olefins cause a small but insignificant interference.	10 ppb in 50 L of air. (23 µg/m ³)	NA	>60 L for one impinger with an efficiency of 95%.	Exposed sample solution stable for 23 h.	21, 42, 61
2. DNPH/HPLC (Dinitro-phenyl hydrazine/high-performance liquid chromatography)	Active collection in impingers containing 0.25% DNPH in aqueous 2 N hydrochloric acid with a hydrocarbon solvent layer. Extraction into dichloromethane. Evaporation to dryness. Dissolution of residue in acetonitrile. Determination by HPLC/UV.	Acetone may interfere.	NA	NA	NA	NA	28, 66
3. Hydroquinone-treated charcoal--GC/FID	Active collection on sorbent comprising Sep-Pak C ₁₈ cartridge coated with DNPH and phosphonic acid. Desorption with acetonitrile, determination by HPLC/UV.	NA	Not determined. Estimated to be <0.3 ppb in 100 L of air. (<0.7 µg/m ³)	NA	NA	NA	13
4. 13X molecular sieves--GC/FID	Active collection on charcoal impregnated with hydroquinone. Extraction with 1,2-dichloroethane. Determination by GC/FID.	NA	20 ppb in 5 L of air. (46 µg/m ³)	Sampling and analysis: 60 to 76% recoveries at 50 to 60 ppb with RSDs of 5 to 6%.	< L/100 ng of sorbent.	Sorbed acrolein stable for 24 day at ambient temperatures, >5 days at -22 °C.	64
5. Four stage sorbent--GC/MS	Active collection on 13X molecular sieves. Desorption with water. Determination by GC/FID.	NA	110 ppb in 8 L of air. (252 µg/m ³)	Analysis: 97 ± 11% recovery of 5- to 8-µg amounts of acrolein. 90 ± 7% recovery of 60- to 200-µg spikes.	8 L/g of sorbent at 100% RH.	Sorbed acrolein stable for 8 weeks at 0 °C.	63
6. 2-Hydroxymethyl piperidine--GC/NPD	Active collection on Amberlite XAD-2 coated with 2-hydroxymethyl piperidine. Desorption with toluene. Determined by GC/NPD.	NA	NA	Sampling and analysis: Tenax-GC, 41% recovery, Porapak Q, 20 to 50%, Ambersorb 340, 11%.	NA	NA	34
				Sampling and analysis: 127% recovery at 55 ppb, 97% recovery at 150 ppb, 100% recovery at 700 ppb. Precision corresponded to a RSD of 11.1%.	NA	Amounts of the acrolein derivative corresponding to 2 to 6 µg of acrolein were stable for up to 28 days.	65

^aCalculated from $\mu\text{g}/\text{m}^3 = \frac{P \cdot (\text{MW}) \cdot (\text{ppb}) \cdot 10^3}{(82.07) \cdot I}$

where

P = pressure in atmospheres

MW = molecular weight

82.07 = gas constant in $\frac{\text{cm}^3 \cdot \text{atm}}{\text{deg. mole}}$

I = absolute temperature (°K)

E. Other Compounds

NITROSAMINES AND NITROSOMORPHOLINE

Nitrosamines are of concern to environmental chemists because they have been shown to be carcinogenic in many animal species. They are formed by the interaction of amines and the nitrite ion or other nitrogen oxides. They have been found in high-protein foodstuffs and in some herbicides and industrial chemicals. Some nitrosamines are also formed during the production of rubber (1). Most analytical-methods development has centered on the determination of nitrosamines in foodstuffs; however, the discovery of nitrosamines in the air of an industrial site (2) and in ambient community air (3) has prompted method development applicable to accurate determination of nitrosamines in ambient air.

Sampling methods

Investigators have used both liquid and solid sorbents for collection of nitrosamines from the air. Cryogenic KOH traps have been used to collect nitrosamines (3-7). Fine et al. (3) found the recovery of dimethylnitrosamine (DMN) to be 43.6% with traps of 1 mL of 1 N KOH. Fisher et al. (6) reported artifact formation of DMN when dimethylamine and NO_x were brought together by cryogenic trapping. The artifact did not occur with ambient-temperature traps. Rounbehler et al. (7) found that the retention of nitrosamines in KOH traps, as well as ascorbic acid traps, is dependent on temperature, sampling time, and the specific nitroso compound. The liquid traps efficiently retain nitrosomorpholine, but the dialkyl nitrosamines are readily lost from these sorbents. Retention decreases for all nitroso compounds as sampling temperature or time are increased.

Rounbehler et al. (7) also evaluated six dry solid sorbents for nitrosamine collection, including activated charcoal, activated alumina, silica gel, Florisil, Tenax-GC, and ThermoSorb/N cartridges. All of the solid sorbents except Tenax-GC retained 100% of the nitrosamines. The dry sorbents, however, with the exception of ThermoSorb/N, were found to be prone to artifact formation of nitrosamines from secondary amines and nitrogen oxides. They concluded that the wet impinger traps are free from artifact formation but lack the ability to quantitatively retain a broad spectrum of volatile nitrosamines. The only sorbent system found to be free of artifact formation and having the desired retaining ability was the ThermoSorb/N cartridges.

Analytical methods

Gas chromatography has proven capable of separating volatile nitrosamines contained in extracts. Most of the research has been channeled into selective and sensitive detection of the separated compounds. One of the first methods for detecting nitrosamines involved oxidizing them to the corresponding nitramines which are extremely sensitive to the ECD (8-11). The response of nitramines to the ECD was greater by two to three orders of magnitude than the response of the parent nitrosamine to the flame-ionization detector (10).

The alkali FID was applied to the direct detection of nitrosamines (12). This detector gives a selective response to nitrogen- and phosphorus-containing compounds. The presence of other nitrogen-containing compounds does cause an interference with the use of this detector.

The development of the thermal-energy-analyzer (TEA) detector, which was more selective for nitrosamines, improved the capabilities for their determination (13). The detector is selective for nitric oxide. The nitrosamines are cleaved at the N-NO bond, and the nitric oxide is detected by its chemiluminescent reaction with ozone. The emission is monitored in the near IR region (14, 15). The selectivity of this detector eliminates many potential interferences. The addition of a cold trap between the TEA catalytic pyrolyzer and the TEA luminescent reaction chamber freezes out many potential interferents (16). The TEA is also extremely sensitive for nitrosamines. Fine et al. (16) demonstrated the detection of less than 1-ng/mL concentrations of several nitrosamines.

Even though the selectivity of the TEA is very good, the problem of artifacts in the determination of nitrosamines still exists (17,18). Rigorous quality-control measures must be followed when low levels are being determined.

Researchers have also used mass-spectrometric detection in conjunction with GC separation to determine nitrosamines. The research in this area through 1978 was reviewed by Gough (1). Selective-ion monitoring is often preferred (2, 19). Investigators have matched the detection limits of the TEA using GC/MS (6, 19,20). This method is free of the artifacts sometimes associated with the TEA (6). However, these artifacts are rare, and the TEA is usually just as reliable as the MS detector (20).

A recent technical report (21) reviews the determination of N-nitroso compounds as applied to the factory environment.

GC combined with either a TEA or MS detector has emerged as the most appropriate analysis method for nitrosamines. Collection on ThermoSorb/N cartridges appears to be the most reliable sampling procedure. Marano et al. (19) used the ThermoSorb/N and both methods of detection to determine N-nitrosodimethylamine (NDMA) and N-nitrosomorpholine (NMOR) in the air near tire-storage locations. The detection limits for the GC/MS method were 35 ng of NDMA and 27 ng of NMOR. The corresponding detection limits using the TEA were 5 ng of NDMA and 8 ng of NMOR. The detection limits for N-nitrosoethylamine and N-nitrosodi-n-butylamine were comparable, but these compounds were not detected in this study. The agreement obtained between the two methods was excellent. Webb et al. (20) compared the two detection methods for the analysis of foodstuff extracts for nitrosamines. Again, in most cases the two techniques agreed very well. The authors suggest using GC/MS for confirming TEA results.

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TABLE 53. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF DIALKYL NITROSAMINES AND NITROSOMORPHOLIN

Method No.	Analyte	Principle	Interferences	Analytical detection limit	Typical sample volume, L	Minimum ^a detectable concentration	Accuracy and precision	Reference
1	DMN	A. Tenax sorbent collection B. GC/MS analysis using SIM (m/e = 74)	A. Dimethylamine plus high concentrations of NO _x B. Breakthrough volume is 224/2.2 g of Tenax-GC at 70 °C	<0.1 ng	120	0.0006 µg/m ³	NA	2
2	DMN, DIN	A. Cryogenic KOH trapping, GC/ILC B. GC/ILC and HPLC/ILC analysis	NA	NA	NA	0.001 µg/m ³	Recovery variable	3, 4, 5
3	DMN	A. Ambient-temperature KOH trapping B. GC/MS analysis using SIM (m/e = 74)	Sunlight destroys trapped DMN. Dimethylamine plus NO _x produces DMN at cryogenic temperatures	.01 ng	100	sub-µg/m ³	NA	6
4	DMN, DIN, DPN, DBN, NNDP	A. B wet or dry sorbents evaluated B. GC/ILC analysis	Amines + NO _x on dry sorbents	NA	240	0.025 µg/m ³	Wet sorbents did not retain nitrosamines. Dry sorbents, except Tenax retained 100%. Recoveries 30-75%.	7
5	DMN, DIN	A. KOH trapping B. Conversion to nitrosamines C. Analysis by GC/ECD	NA	0.05 ppb	180	<0.5 µg/m ³ (<0.05 ppb)	Recoveries 30-75%.	11
6	DMN, DIN, DPN, DBN, NNDP	A. Collection on ThermoSorb/N B. GC/MS with Unikon concentrator and GC/ILC analysis	NA	20-40 ng using GC/MS; 5-10 ng using GC/ILC	300	0.1-0.2 µg/m ³	Reproducibility within 5%	19

^aFrom the reference listed.

PROPYLENE OXIDE

Propylene oxide (methyloxirane, 1,2-epoxypropane) is a colorless, flammable, low-boiling liquid. It is miscible with most organic solvents but forms a two-layer system with water (1). Propylene oxide (PO) has an odor that is described as sweet, alcoholic, and like natural gas, ether, or benzene (2). PO boils at 34.2 °C at 760 mmHg. It is miscible with acetone, benzene, carbon tetrachloride, ether, and methanol. It is used largely for the production of propylene glycol and its derivatives. Substantial quantities are used in the preparation of hydroxypropyl celluloses and sugars, surface-active agents, isopropanolamine, and a host of other chemicals. It is also used as a fumigant, herbicide, preservative, and in some cases, as a solvent. PO is highly reactive chemically, being intermediate between ethylene oxide and butylene oxide. The liquid is relatively stable but can react violently with materials having a labile hydrogen, particularly in the presence of catalysts. The hazard to health of PO is not as great as that of ethylene oxide, but it is recognized by NIOSH as being a toxic substance. Therefore, the permissible exposure limit (PEL) and the TLV have been set at 100 ppm and 20 ppm respectively (2).

Absorption on charcoal, desorption with carbon disulfide, and determination by GC/FID is NIOSH's present recommended method for propylene oxide in the atmosphere (3). The method was validated over the range of 121 to 482 mg/m³ at a temperature and pressure of 24 °C and 766 mm of mercury using a 5-L sample (4). The Coefficient of Variation (CV_T) for the total analytical and sampling method over the validated range was 0.085. An advantage of the method is that the sampling device is small, portable, and involves no liquids. Also, interferences are minimal, and most of those which do occur can be eliminated by alternating the GC conditions. One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes.

In a similar procedure to the NIOSH method, Porapak N is used for adsorption of propylene oxide (4). The PO is eluted by placing the tube with the Porapak N directly into the carrier gas stream of the chromatograph, and the tube is heated to 200 °C. Advantages of the technique are ppb sensitivity and quantitative recovery. One disadvantage of the method is that high humidity may cause peak broadening and somewhat shorter retention times. This effect, which concerns the chromatographic column and not the sampling tube, may be compensated by using mass-spectrometric detection or by spiking a sampling tube with a standard to aid in peak identification.

A method was developed for determination of PO in air by GC/FID using Porapak Q as the collection device (5). The method is sensitive to 0.0001 µg in a 5-mL sample with a relative error of 8%. The major disadvantage of the method is that the PO was not stable on Porapak Q after 6 h.

An IR analyzer is one of the most useful portable monitors for propylene oxides. The instrument is calibrated for a wavelength of 12.0 µm for PO. Propylene oxide is brought into the gas-sample cell by means of an

integral sample pump and is exposed to IR light. The gas-sample cell has sufficient pathlength for sensitivity, and the resulting absorbance is indicated on a meter calibrated directly in ppm. The limit of detection is 0.3 ppm (6).

Presently, the NIOSH method is the best procedure for determination of PO in air. The charcoal tubes can be analyzed by means of a quick, instrumental method. Also, the method is sensitive enough to detect the present OSHA standard. However, further work is needed to obtain ppb and sub-ppb levels.

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TABLE 34. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF PROPYLENE OXIDES

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum detectable concentration	Accuracy and precision	References
1	A. Collection on charcoal B. Desorption with CS ₂ C. Determination by GC/FID	Compounds with similar retention times	1-5 ng	5	1.21x10 ⁻⁵ µg/m ³ ^a	(CV) _r = 0.085	3
2	A. Collection on Porapak N B. Heat desorption B. Determination by GC/FID	High humidity	1-5 ng	1	3.3 µg/m ³ ^b	NA	4
3	A. Collection on Porapak Q B. Determination by GC/FID	Compounds with similar retention times	NA	NA	NA	NA	5
4	Infrared analyzer	NA	NA	NA	700 µg/m ³ ^b	NA	6

^aThis is the lower limit of the validated range as given in reference 3 and is not necessarily the lower limit of detection.

$$b \text{ Calculated from } \mu\text{g}/\text{m}^3 = \frac{P \cdot (\text{MW}) \cdot (\text{ppb}) \cdot 10^3}{(82.07) \cdot I}$$

where

P = pressure in atmospheres

MW = molecular weight

82.07 = gas constant in $\frac{\text{cm}^3 \cdot \text{atm}}{\text{deg. mole}}$

I = absolute temperature (°K)

GLYCOL ETHERS

The monoalkyl ethers of ethylene glycol are usually colorless and almost odorless liquids. Their boiling points and refractive indices increase with molecular weight; their specific gravities decrease. They are miscible with most organic solvents. The lower members up to butyl ether are completely water soluble (1). Recent studies have shown that 2-methoxyethanol and 2-ethoxyethanol cause adverse reproductive effects in male and female workers. OSHA maximum TWA for an 8-h exposure is 80 mg/m³ (25 ppm) for 2-methoxyethanol and 740 mg/m³ (200 ppm) for 2-ethoxyethanol. The acetate esters of 2-methoxyethanol and 2-ethoxyethanol have shown similar toxic results (2).

Various sampling methods have been used for glycol ethers ranging from sorbent-tube collection using sampling pumps to passive collection with diffusion monitors and dosimeters. The samples were usually analyzed by GC/FID.

There are two methods described for glycol ether collection on charcoal tubes. In one procedure outlined by Langhorst (3), several glycol ethers collected on charcoal tubes are desorbed with a two-phase eluent consisting of 5 mL of carbon disulfide and 5 mL of water. Both layers are analyzed by GC/FID on a column packed with 2.5% Oronite NIW on 60/80-mesh Carbopak B.

The method was validated for both short-term (15-min) and long-term (8-h) time-weighted averages. Detection limits are in the 5-µg/sample (1 ng/injection) range for most of the ethers evaluated. Relative precision at the 95% confidence level averaged 16.3%. The other charcoal-tube procedure outlined in NIOSH Method No. S79 is for 2-methoxyethanol and 2-butoxyethanol (4). It involves extraction with 0.5 mL of a 5% methanol in methylene chloride solution and analysis by GC/FID on a column packed with 10% FFAP on 80/100-mesh Chromosorb W (AW-DMCS). This method was validated over the range of 44 to 160 mg/m³ for 2-methoxyethanol and 124 to 490 mg/m³ for 2-butoxyethanol.

The collection of glycol ethers on a silica-gel tube and analysis by GC/FID is described by Langhorst (3). After collection the silica-gel tube is desorbed with 5 mL of a 25% methanol in water solution and analyzed on a column packed with 2.5% Oronite NIW on 60/80-mesh Carbopak B. Long-term sampling of the silica-gel tube under high-humidity conditions may result in breakthrough of some of the more volatile glycol ethers. Detection limits are in the 6-µg/sample (2-ng/injection) range. Relative precision averaged 15.7% RSD.

The collection of 2-methoxyethanol and 2-ethoxyethanol using diffusive monitors is described by Hamlin et al. (5). The monitors are stainless steel tubes approximately 0.25 in. in diameter packed with a suitable absorbent. After collection the monitors are thermally desorbed into a GC/FID containing a column packed with 10% SP-1000 on Chromosorb W (AW). The method is automated by using an automatic sample handler to introduce the sample onto the GC column. Concentrations as low as 0.1 ppm are determined during a 5-h sampling period.

The collection of 2-methoxyethanol, 2-ethoxyethanol, and 1-methoxypropanol on 3M Organic Vapor Monitor Badge is described by Langhorst (3). After collection the charcoal pad is removed and desorbed with 2 mL carbon disulfide plus 2 mL distilled water. The water layer is analyzed by GC/FID on a column packed with 5% SP-1000 on 60/80-mesh Carbopak B. Detection limits are in the 5- μ g/badge range. Sensitivities may be inadequate for sampling periods less than 1 h. Relative precision averaged 14.9% RSD for the three ethers evaluated.

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TABLE 35. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF GLYCOL ETHERS

Method No.	Analyte	Principle	Potential Interferences	Analytical detection limit	Typical sample volume, L	Minimum ^a detectable concentration	Accuracy & precision	Reference
1	2-methoxyethanol	A. Collection on charcoal tube B. Desorption with 5% methanol in CH ₂ Cl ₂ C. Determination by packed-column GC/FID	A. High humidity B. Compounds with a similar GC retention time to 2-methoxyethanol	1-5 ng per injection	50	4.4 x 10 ⁴ µg/m ³ b	RSD ± 7.2%	4
2	2-methoxyethanol 2-ethoxyethanol	A. Collection with a diffusive monitor B. Thermal desorption C. Determination by packed-column GC/FID on a 10% SP 1000 on Chromosorb W column	A. Compounds with a similar GC retention time to 2-methoxyethanol and 2-ethoxyethanol	1-5 ng per injection	NA	370 µg/m ³ c	NA	5
3	Glycol ethers	A. Collection on a charcoal tube B. Desorption with 5 mL H ₂ O + 5 mL CS ₂ C. Determination by packed-column GC/FID	A. Compounds with a similar GC retention time to glycol ether	1-5 ng per injection	NA	200-500 µg/m ³	±1% to ±18%	3
4	Glycol ethers	A. Collection on a silicone-gel tube B. Desorption with 25% methanol in H ₂ O C. Determination by GC/FID	A. High humidity. B. Compounds with a similar GC retention time to glycol ether	1-5 ng per injection	NA	200-500 µg/m ³	±1% to ±18%	3
5	Glycol ethers	A. Collection on a 6-µm dosimeter B. Desorption with 2 mL CS ₂ + 2 mL H ₂ O C. Determination by GC/FID	A. Compounds with a similar GC retention time to glycol ether	1-5 ng per injection	NA	200-500 µg/m ³	NA	3

$$^a \text{Calculated from } \mu\text{g/m}^3 = \frac{P \cdot (MW) \cdot (\text{ppb}) \cdot 10^3}{(82.07) \cdot I}$$

where

P = pressure in atmospheres

MW = molecular weight

82.07 = gas constant in $\frac{\text{cm}^3 \cdot \text{atm}}{\text{deg. mole}}$

I = absolute temperature

^bThis is the lower limit of the validated range as given in reference 4 and is not necessarily the lower limit of detection.

^cThis is the lower limit of the validated range as given in reference 5 and is not necessarily the lower limit of detection.

p-DIOXANE

Dioxane ($C_4H_8O_2$) is a colorless liquid miscible with water and most organic solvents. The odor of dioxane in low concentrations is faint and generally inoffensive and has been described as being somewhat alcoholic. It is hygroscopic, and because of its ether linkages, it produces peroxides and other degradation products upon standing in the presence of moisture. Dioxane is a poisonous substance with acute and chronic effects. Animal studies show that dioxane may be considered a weak-to-moderate carcinogen to animals at high dosage levels. The liquid is painful and irritating to the eyes and skin. Dioxane vapor has poor warning properties and can be inhaled in amounts that may cause serious systematic injury, principally in the liver and kidney areas (1). Because of the toxic effects of dioxane, the OSHA maximum TWA is 100 ppm for an 8-h exposure (2).

Dioxane in the atmosphere has been successfully determined by using NIOSH Method P&CAM 127. This method involves collecting organic solvents including dioxane on charcoal tubes. After collection, the tube is desorbed in 0.5 mL of carbon disulfide and determined by GC/FID. The limit of detection is 0.05 mg/sample in an 18-L sample. The mean relative standard deviations of the analytical method and the analytical and sampling method are 8% and 10% respectively. One advantage of the method is that the sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick instrumental method. One disadvantage of the method is the amount of sample which can be taken is limited by the number of milligrams the tube will hold before overloading. Also, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise because the pump is usually calibrated for one tube only (3).

Determination of dioxane by NIOSH Method S360 is very similar to NIOSH Method P&CAM 127. Dioxane is collected on charcoal tubes. The charcoal tube is desorbed with 1 mL of carbon disulfide, and dioxane is determined by GC/FID. The method was validated over the range of 155 to 651 mg/m³ at an atmospheric temperature and pressure of 21.5 °C and 754 mmHg, using a 10-L sample. The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 155 to 651 mg/m³ was 0.054. This value corresponds to a 19-mg/m³ standard deviation at the OSHA standard level. One advantage of the method is that the sampling device is small, portable, and involves no liquids. Also, the tubes are analyzed by means of a quick instrumental method. One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams the tube will hold before overloading. Also, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. Furthermore, when water is present in great amounts, condensation occurs in the charcoal tube, and organic vapors are not trapped. High humidity also decreases the breakthrough volume (4).

The collection of dioxane on charcoal followed by heat desorption is an alternative method to the NIOSH methods. The dioxane is desorbed from the charcoal and condensed in a liquid-nitrogen-cooled trap prior to introduction into the GC/MS for identification and quantification (5).

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TABLE 36. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF p-DIOXANE

Method No.	Analyte	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum detectable concentration	Accuracy and precision	References
1	Dioxane	A. Collection on charcoal B. Desorption with 1 mL of CS ₂ C. Determination by GC/FID	A. Compounds with similar retention times to dioxane	1-5 ng per injection	18	2.8x10 ³ µg/m ^{3a}	10% RSD	3
2	Dioxane	A. Collection on charcoal B. Desorption with 1 mL of CS ₂ C. Determination by GC/FID	A. Compounds with similar retention times to dioxane B. Water vapor reduces adsorbent capacity	1-5 ng per injection	10	1.55x10 ⁵ µg/m ^{3b}	NA	4
3	Dioxane	A. Collection on charcoal B. Heat desorption C. Determination by GC/MS	A. Water vapor reduces adsorbent capacity	1-20 ng	240	0.004-0.08 µg/m ^{3c}	NA	5

^aThis is the lower limit of the validated range as given in reference 3 and is not necessarily the lower limit of detection.

^bThis is the lower limit of the validated range as given in reference 4 and is not necessarily the lower limit of detection.

^c Minimum detectable amount $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$

ACRYLONITRILE

Acrylonitrile is a colorless to pale-yellow liquid with an odor that resembles peach seeds. It solidifies at -84°C and boils at 77°C . It is very reactive and polymerizes readily. It is classified as a cocarcinogen, and the OSHA TLV is 2 ppm (1,2).

Sampling methods for acrylonitrile are based on collection of the compound on a sorbent or cryogenic trapping. Analysis of the sample uses GC with a variety of detectors including FID and MS.

The collection of acrylonitrile using a CMS sorbent tube, followed by thermal desorption into a cryogenic trap and analysis by GC/MS using capillary columns has been described in a recent EPA document (Method T02) (3). The sampling procedure and the analytical method can be automated in a reasonable, cost-effective manner. The analytical detection limit is between 1 and 20 ng, depending on the mass-spectral conditions chosen. Multiple samples are easily taken and are transported easily. The use of high-resolution capillary columns combined with detection by MS offers a high degree of specificity for acrylonitrile. Compounds having a similar mass spectrum and GC retention time to acrylonitrile will interfere with the method. The analyst must take extreme care in the preparation, storage, and handling of the CMS cartridges throughout the entire sampling-and-analysis procedure to minimize contamination problems. The reproducibility of the method was found to be $\pm 25\%$ on parallel tubes, but has not been completely validated.

NIOSH method P&CAM 204 (4) utilizes the adsorption of acrylonitrile onto Carbosieve. The NIOSH method uses methanol desorption and GC/FID detection. The sensitivity of the method is in the ppm range because of the 1 mL extraction volume. A second NIOSH method (15) and a method by Marano et al. (6) uses charcoal to collect acrylonitrile. The tubes are then extracted with methanol. Marano used GC/NPD to detect 10 pg of acrylonitrile per injection, and the NIOSH method used GC/FID to detect 4.5 mg/m^3 per sample.

Several workers have used other sorbents to trap acrylonitrile. Tenax-GC (7,8,9) has a low breakthrough volume ($<5\text{ L/g}$) for acrylonitrile. However, it is a popular sorbent. Porapak N (10) has also been used to collect acrylonitrile but is also somewhat limited by breakthrough volume (5 L/g).

Cryogenic trapping is a sampling technique that is applicable when small samples ($<3\text{ L}$) can be utilized. The methods (11,12) provide low-nanogram detection limits but are hampered by the collection of water in the traps.

Passive samplers for acrylonitrile using Tenax-GC sorbents have not been very successful (13). The problem with a Tenax-GC passive sampler was the low sample capacity (0.3 L/g) found in the study. The preparation and determination by GC/MS of in situ standards of acrylonitrile has also been discussed in the literature (14).

Sampling with a carbon-based sorbent followed by detection with GC/MS or GC/NPD offers the possibility of low detection limits and high sample capacity.

The technique based on the EPA method (3) needs to be explored further and validated.

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TABLE 37. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF ACRYLONITRILE

Method No.	Principle	Potential Interferences	Analytical detection limit	Typical sample volume, L	Minimum ^a detectable concentration	Accuracy & precision	References
1	A. Collection on Carbasieve B. Heat desorption C. GC/MS	A. Contamination of sorbent B. Compounds with a similar mass spectrum and GC retention time to acrylonitrile	1-20 ng	100	0.01-0.2 µg/m ³	18% RSD 85% recovery	3
2	A. Collection in cryogenic trap B. GC/FID	A. Ice forming in trap B. Compounds with a similar GC retention time	1-5 ng	1	1-5 µg/m ³	5% RSD 90% recovery	11
3	A. Collection on Tenax-GC B. Heat desorption C. GC/FID or GC/MS	A. Contamination of sorbent B. Breakthrough volume <1.25 L C. Compounds with a similar GC retention time	1-5 ng	1	1-5 µg/m ³	NA	7,8,9
4	A. Collection on charcoal B. Methanol desorption C. GC/NPD	A. Nitrogen- or phosphorus-containing compounds with a similar GC retention time to acrylonitrile B. CS ₂	0.01 ng per injection	NA	NA	1% RSD	6
5	A. Collection on cryogenic trap B. GC/packed/capillary (2-dimensions)/PID/FID and GC/MS	A. Butanol B. Breakthrough volume <2-3 L C. Compounds with a similar GC retention time	Low ng range	2	Low µg/m ³ range	NA	12
6	A. Collection on Carbasieve B B. Methanol desorption C. GC/FID	A. High humidity B. Compounds with similar retention times	100 µg per sample	20	4.0x10 ⁻⁴ µg/m ³ ^b	5% RSD 90% recovery	4
7	A. Collection on charcoal tube B. Methanol desorption C. GC/FID	A. Water B. Compounds with similar retention times	1-5 ng per injection	20	1.75x10 ⁻⁴ µg/m ³ ^c	7% RSD 94% accuracy	5

^a Minimum detectable concentration $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ ng}}$ unless otherwise stated.

^b This is the lower limit of the validated range as given in reference 4 and is not necessarily the lower limit of detection.

^c This is the lower limit of the validated range as given in reference 5 and is not necessarily the lower limit of detection.

HEXACHLOROCYCLOPENTADIENE

Hexachlorocyclopentadiene is a nonflammable liquid which has a pungent, musty odor. Hexachlorocyclopentadiene is commercially important as an intermediate for many insecticides, polyester resins, and flame retardants. It has a boiling point of 239 °C, is toxic, and is readily absorbed through the skin (1).

A method for the determination of hexachlorocyclopentadiene in air has been published by NIOSH (2). In this method a known volume of air is drawn through a tube containing Porapak T to trap the hexachlorocyclopentadiene present. The Porapak T is then transferred to a small vial and extracted with hexane. An aliquot of the sample is then analyzed by GC/ECD. The breakthrough volume of hexachlorocyclopentadiene on the sorbent tube was found to be greater than 100 L with a sampling rate of 0.2 L/min at a hexachlorocyclopentadiene concentration of 0.4 mg/m³ and at a relative humidity of greater than 90%. The detection limit is 25 ng/mL of extracting solvent. Compounds having the same retention time as hexachlorocyclopentadiene will interfere with the method.

A second method for the analysis of hexachlorocyclopentadiene has appeared in the literature (3). A known volume of air is passed through an impinger containing an organic solvent, and then an aliquot of the solution is analyzed by GC/ECD. Benzene was found to be a better solvent than hexane. Recovery at ambient temperatures was reported to be quantitative at the 1-ppb level in air. The main problem with this method is the evaporation of the solvent from the impinger. No validation study has been performed on this method.

At the present time the Environmental Protection Agency has not proposed a method for the analysis of hexachlorocyclopentadiene in air. The NIOSH method is sensitive into the ppb range. The selectivity and sensitivity of this method can be improved by using capillary columns and GC/MS. More work needs to be done in this area.

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TABLE 38. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF HEXACHLOROCYCLOPENTADIENE

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volumes, liters	Minimum detectable concentration	Accuracy and precision	References
1	A. Adsorption onto Porapak I	A. Compounds having a similar GC retention time to hexachlorocyclopentadiene	25 ng in 1 mL hexane extract	3	13 $\mu\text{g}/\text{m}^3$ ^{3a}	$\pm 8\%$	2
	B. Desorption with hexane						
	C. Analysis by GC/ECD	B. Contamination of the Porapak I tube with hexachlorocyclopentadiene					
2	A. Air is passed through an impinger containing hexane or benzene	A. Evaporation of the solvent	1.5 x 10 ⁻³ ng per injection	2	11 $\mu\text{g}/\text{m}^3$ ^{3b}	NA	3
	B. An aliquot of the solution is analyzed by GC/ECD	B. Compounds having a similar GC retention time to hexachlorocyclopentadiene					

^aThis is the lower limit of the validated range as given in reference 2 and is not necessarily the lower limit of detection.

$$\text{b Calculated from } \mu\text{g}/\text{m}^3 = \frac{P (\text{MW}) (\text{ppb}) (10^3)}{(82.07) I}$$

where

P = pressure in atmospheres

MW = molecular weight

82.07 = gas constant in $\frac{\text{cm}^3 \text{ atm}}{\text{deg. mole}}$

I = absolute temperature (K)

MALEIC ANHYDRIDE

Maleic anhydride ($C_4H_2O_3$) is commercially available as a white crystalline solid or a fused block. Maleic anhydride is miscible with most organic solvents, has a boiling point of 202 °C, and reacts violently with alkali metals. When dissolved in water or alcohols, maleic anhydride forms maleic acid and esters. Naphthalene, *o*-xylene, *n*-butene-1, and other similar compounds can oxidize to form maleic anhydride. Maleic anhydride is a powerful irritant to skin, eyes, and mucous membranes. Inhalation of maleic anhydride vapor can cause pulmonary edema. OSHA has established a time-weighted average (TWA) of 1.0 mg/m³ (0.25 ppm) for an 8-h exposure (1).

Brown and Purnell (2) have evaluated the use of Tenax-GC as a collection medium for maleic anhydride in the atmosphere. The effects of humidity, sampling rate, and sampling temperature were studied. Maleic anhydride is retained well by Tenax-GC and has a safe sampling volume of 440 L/g of sorbent at ambient temperature. After sample collection the Tenax-GC tubes were thermally desorbed at 160 °C and analyzed by GC/FID.

In NIOSH Method P&CAM 302, atmospheric maleic anhydride is collected in a midget bubbler containing 15 mL of water. Maleic anhydride hydrolyzes immediately to maleic acid when in contact with water. Maleic acid is then analyzed by HPLC with UV detection at 254 nm. The limit of detection is estimated to be 50 ng per injection, and the relative standard deviation is in the 6.3% range (3). The precision of the method is limited by the reproducibility of the pressure drop across the bubbler. This drop will affect the flow rate and cause the measured sampling volume to be imprecise. This method has several disadvantages. Bubblers are difficult to ship and are easily broken. Also, this method cannot distinguish between maleic anhydride and maleic acid.

Several GC methods have been used to determine maleic anhydride as a reaction product from the air oxidation of *n*-butene-1, *o*-xylene, or naphthalene (4-7). Maleic anhydride was either collected in an organic solvent trap and then analyzed by GC or was collected and analyzed directly on the GC column. The relative errors of these methods ranged from 3 to 10%. The concentration of maleic anhydride in copolymers has been determined using a potentiometric method by Raetzsch and co-workers (8).

At the present time no routine, validated analysis method exists for maleic anhydride. The method based on collection on Tenax-GC is promising but further work is needed.

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TABLE 39. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF MALEIC ANHYDRIDE

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volumes, Liters	Minimum ^a detectable concentration	Accuracy and precision	References
1	A. Collection on Tenax-GC B. Thermal desorption into a cryogenic trap C. Analysis by GC/FID	A. Compounds having similar retention time B. Contamination of Tenax-GC with the compound of interest C. Safe sampling volume = 440 L/g	1-5 ng	440	0.002-0.01 µg/m ³ ^a	NA	2
2	A. Collection in a midjet bubbler containing 15 mL of H ₂ O B. Hydrolysis of maleic anhydride to maleic acid C. Determination by HPLC/UV at 254 nm	A. Compounds having similar retention time to maleic acid B. Method cannot differentiate between maleic anhydride and maleic acid	50 ng per injection	360	500 µg/m ³ ^b	6.3% RSD	3
3	A. Collection in an organic solvent or directly onto GC column B. Analysis by GC/FID	A. Compounds having similar retention time to maleic acid	NA	NA	NA	±10%	4,5,6,7

^a Minimum detectable concentration $\left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Analytical detection limit, ng}}{\text{Typical sample volume, L}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \mu\text{g}}{1000 \text{ mg}}$ unless otherwise stated.

^b This is the lower limit of the validated range as given in reference 3 and is not necessarily the lower limit of detection.

ETHYLENE OXIDE

Ethylene oxide (1,2-epoxyethane) is a colorless flammable gas or liquid. It condenses to a liquid at 10.4 °C at 760 mmHg. It is miscible in water, alcohol, ether, and many other organic solvents. Ethylene oxide (EO) is highly reactive and is used to manufacture many chemicals, including ethylene glycol, acrylonitrile, and nonionic surfactants (1). Ethylene oxide is widely used as a bactericide, fumigant, sterilant, and insecticide. It is used in hospitals either alone or in combination with carbon dioxide or Freon 12 for sterilization. EO production in the United States is approximately 6 billion pounds per year (2). Approximately 99.5% of the EO is used in the chemical industry and the remaining 0.5% is used as a sterilant in hospitals.

Numerous air-sampling-and-analysis methods have been developed for EO in ambient air. Some of these methods are suitable or can be adapted to source monitoring. The major obstacles to overcome in sampling-and-analysis methods are imposed by the volatility and reactivity of EO. The volatility of EO limits both the selection of suitable sorbents and the total volume of air that may be sampled without the loss of EO. The reactivity further limits the selection of sorbents. However, the reactivity of EO is used to advantage in some methods that are based on the rapid and complete reaction of EO to form a stable compound suitable for analysis. Other sampling and analysis methods are available to determine EO directly. These sampling and analysis devices are direct monitors that do not rely on concentration, desorption, or reaction techniques. Air samples are injected without concentration into the GC column. Portable infrared analyzers can measure transient peak concentrations and ambient concentrations and operate with little attention.

All methods--both reactive and direct--are summarized in Table 40. A detailed discussion of each method is given below.

NIOSH Method S286 for the collection and analyses of ethylene oxide uses a sampling tube containing 400 mg of activated charcoal and a back-up tube of 200 mg of charcoal. The method was validated over a range of 22 to 98 ppm and has a probable useful range for a 5-L air sample of 11 to 150 ppm (3). Pilney and Coyne (4) improved this method by using 1-g charcoal, and they further explored the use of two 600-mg charcoal tubes in series. They used an MSA C-210 mass flow pump at a flow rate of 50 mL per minute and a concentration of 15.6 ppm of EO. Breakthrough was observed after 5 h with the single 600-mg tube, but no breakthrough occurred when two 600-mg tubes were used in series. Ethylene oxide is desorbed with carbon disulfide and analyzed by GC/FID using a 10-ft x 1/8-in. stainless steel column packed with Porapak QS.

Ethylene oxide is a highly reactive gas. In developing a sound sampling procedure for such a reactive gas, several parameters such as choice of collection materials, its absorption capacity, desorption efficiency, humidity, sampling rate, sample volume, and shelf life should be investigated. Ozai and Ketcham (5) evaluated six noncarbon and nine activated carbon sorbents. The percent recovery data showed that noncarbon adsorbents were not suitable for collecting EO in air. The activated carbons gave variable recoveries and migration within the tubes. After several experiments Columbia JXC activated

carbon was selected because it showed promising recoveries. EO was desorbed from the carbon by carbon disulfide and analyzed by (GC/FID). Columns were evaluated, and two columns (Tergital TMN or UCON LB550X) were found suitable for EO analyses. The lower detection limit of the method is 0.15 ppm in a 10-L air sample. Furthermore, other contaminants that may be present with EO such as formaldehyde, vinyl chloride, vinyl acetate, ethylene glycol, propylene oxide, acrolein, propionaldehyde, ethanol acetaldehyde, and ethylene dichloride will not normally interfere.

Romano and Rinner (2) used impingers containing 0.1 N sulfuric acid to collect ethylene oxide. The ethylene oxide is converted to ethylene glycol and the glycol is determined by GC.

Impregnating activated carbon with sulfuric acid and using this as a collection medium in sorbent tubes promises possibilities of an enhanced sampling method and is now under investigation.

GC as a means for rapid determination of EO in air has been investigated. Collins and Barker (6) used a portable GC (Photovac 10A10) with a highly sensitive photoionization detector. EO was analyzed on a 2 ft x 1/8-in. Teflon column packed with microfine carbon. EO was quantified at ambient-air concentrations by operating the column at ambient temperature and using peak height measurements. Of more significance, the level of detection was 0.1 ppm, the retention time for EO was less than 2 min, and the instrument was suitable for 24-h monitoring. The Photovac 10A10 gas chromatograph was operator-dependent; however, autosampling is possible. For continuous monitoring, a fully automated air-monitoring system was described (6). The sensitive Photovac 10A10 gas chromatograph designed to analyze low concentrations (0.001 to 100 ppm) of EO was found to work equally well at higher levels used for fumigants (7).

A gas chromatograph equipped with a thermistor cell was investigated by Dumas (8) for determination of ethylene oxide in air. The sample size was 5 mL, and it was injected directly on the column. The limitation of this method lies in the detection limit. It requires 1 µg/mL in air to give full-scale detection. This method is not suitable for ambient-air monitoring.

Vanell (9) described a portable infrared analyzer. He found that the most useful portable monitor for EO is an infrared analyzer calibrated for a wavelength specific to ethylene oxide. Air containing EO is brought into the IR cell by means of a sampling pump. A meter reads the concentration of EO in parts per billion.

Absorption of ethylene oxide on activated carbon, desorption with carbon disulfide, and determination by GC/FID is the present method of choice. This method has a detection limit of 4 ng per injection with good recovery and good precision. At 0.5 and 5.0 ppm, statistical evaluation showed an average recovery of 97% with precision (relative standard deviation) and systematic error of 3.76 and 2.9% respectively.

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TABLE 40. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF ETHYLENE OXIDE

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volumes, L	Minimum ^a detectable concentration	Accuracy and precision	References
1	A. Collection on charcoal B. Desorption with CS ₂ C. Determination with GC/FID	Compounds with similar retention time	1-5 ng per injection	5	4.1x10 ⁻⁴ µg/m ³	CV _I = 0.103	3
2	A. Collection on Columbia JXC activated carbon, B. Desorption with CS ₂ C. Determination with GC/FID	Compounds with similar retention time	4 ng per injection	10	270 µg/m ³	97% recovery in ppm range	5
3	A. Collection in impingers containing 0.1 N H ₂ SO ₄ B. EO converted to ethylene glycol C. Determination by GC	Compounds with similar retention time	NA	NA	360 µg/m ³	94.2% recovery	2
4	GC with photoionization detector	Compounds with similar	NA	0.001	<180 µg/m ³	NA	6

^aCalculated from $\mu\text{g}/\text{m}^3 = \frac{P (\text{MW}) (\text{ppb}) (10^3)}{(82.07) I}$
where

P = pressure in atmospheres
 MW = molecular weight
 82.07 = gas constant in $\frac{\text{cm}^3 \text{ atm}}{\text{deg. mole}}$
 I = absolute temperature (K)

EPICHLOROHYDRIN

Epichlorohydrin (1-chloro-2,3-epoxypropane) is an important solvent in the production of resins. An important constituent of epoxy resins is synthesized by alkylating bisphenol A with epichlorohydrin (ECH). ECH is also used in the manufacture of pharmaceuticals, insecticides, agricultural chemicals, textile chemicals, coatings, adhesives, ion-exchange resins, solvents, plasticizers, nail enamels, glycidyl ethers, surface active agents, and many other chemicals (1). In 1978, the domestic production of ECH was approximately 500 million pounds. It is not surprising, therefore, that many occupations offer possible exposure and many industries use products that are known or suspected to contain ECH. (2)

ECH is a colorless liquid with a characteristic chloroform-like, irritating odor. It boils at 117.9 °C at 760 mmHg. In general, ECH is miscible with ethers, alcohols, carbon tetrachloride, benzene, chloroform, and trichloroethylene. It causes CNS depression; irritation of the skin, eyes, and respiratory tract; and possibly sensitization. ECH is readily absorbed through the skin and is considered extremely toxic. Because of recent inhalation studies on rats and epidemiologic studies on exposed workers, industrial hygienists indicate that ECH should be considered carcinogenic (3). Therefore, a TLV for ECH in workroom air in the United States was set by NIOSH at 2 mg/m³ (0.5 ppm), which was determined as a TWA concentration for up to a 10-h workday in a 40-h workweek (2).

The sampling and analysis of ECH at the ppm to ppb level is generally based on adsorption techniques and gas chromatography. Determination at the ppb level has been reported using GC/MS (1). The analysis by GC uses a variety of detectors including FID, ECD, and MS (2). Activated charcoal is recommended by NIOSH for sample collection (3). Amberlite XAD-2, a styrene divinyl benzene polymer, and XAD-7, an acrylic ester-type polymer, have been used for sampling ECH in air (1).

The colorimetric determination of ECH in air has also been widely used (4). ECH is hydrolyzed to glycerol, oxidized by HIO₄ to formaldehyde in the presence of H₂SO₄, and titrated with chromotropic acid to produce a color. The colorimetric method is generally useful in specific environments for routine work when interferences have been shown to be absent. Acetone and phenol cause severe interference in the colorimetric procedure.

A detailed sampling-and-analytical method for ECH is described in the NIOSH Manual of Analytical Methods, 3d ed. (5), as NIOSH Method No. 1010. The sampler is a sorbent tube containing coconut-shell charcoal. Air is sampled at flow rates from 10 mL to 200 mL/min. The collected sample is reported to be stable for at least two weeks. The applicable range is 2 to 60 mg/m³ (5), which is higher than may be required for ambient-air monitoring. The measurement technique is GC/FID. The ECH is desorbed with CS₂ and analyzed on a Chromosorb 101 column at 135 °C. The NIOSH method has been validated and is in wide use.

NIOSH Method S118 (6) is a similar method to NIOSH Method 1010 for sampling and analysis of ECH. This method involves the adsorption of ECH on a coconut-charcoal tube and desorbing the tube with carbon disulfide. An aliquot of the desorbed sample is then determined by GC/FID using a 10 ft x 1.8-in. stainless steel column packed with 10% FFAP on 80/100-mesh, acid-washed DMCS Chromosorb W. The ECH at the OSHA standard, 0.38 mg, was stable on coconut charcoal for six days at ambient temperature. One advantage of the method is that the sampling device is small, portable, and involves no liquids. The major disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams the tube will hold before overloading. Also, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise.

A sampling method has been evaluated in Sweden using Rohm and Haas Amberlite resins (1). This study compared the results of adsorption of ECH on charcoal and Amberlite XAD-2 (1) with the results of a study using XAD-7. The resin was precleaned, dried, and used to fill small glass tubes, 5 by 0.4 cm. Air was sampled at 0.2 L/min. ECH was desorbed with CS₂ (or CH₂Cl₂) and analyzed by GC/FID on a 0.2% Carbowax 1500 on Carbopack C column at 85 °C. The recovery of ECH from XAD-2 was poor (≈47%); however, the recoveries from XAD-7 were better than or equivalent to those obtained with charcoal. The sampled compound was also found to be stable on XAD-7 during storage of the tubes.

NIOSH Method No. 1010 is the best available method for the determination of ppm levels of ECH in air. The major problems with this method lie in the use of charcoal, which is universally a good adsorbent and therefore likely to concentrate other compounds from ambient-air samples that may interfere in the GC/FID analyses. Also, the 1-mL extraction volume limits the overall detection limit of the method. Alternative recommendations would be to use high-resolution GC/FID, GC/MS, or to further evaluate the sorbent XAD-7. EPA Methods T01, T02, and T03 have not been evaluated for ECH, but may offer detection limits in the ppb and sub-ppb ranges.

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TABLE 41. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF EPICHLOROHYDRIN

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volume, L	Minimum detectable concentration	Accuracy and precision	References
1	A. Collection on charcoal	Compounds with similar retention time	1-5 ng per injection	20	$1.2 \times 10^{-4} \mu\text{g}/\text{m}^3$ ^a	RSD = 3.1%	5
	B. Desorption with CS ₂						
	C. Determination by GC/FID on Chromosorb 101						
2	A. Collection on XAD-7	Compounds with similar retention time	1-5 ng per injection	5	NA	Recovery 99% RSD = 2%	1
	B. Desorption with CH ₂ Cl ₂						
	C. Determination with GC/FID						
3	A. Collection on charcoal	Compounds with similar retention time	1-5 ng per injection	20	$1.17 \times 10^{-4} \mu\text{g}/\text{m}^3$ ^b	RSD = 5.7%	6
	B. Desorption with CS ₂						
	C. Determination with GC/FID on FFAP column						

^aThis is the lower limit of the validated range as given in reference 5 and is not necessarily the lower limit of detection.

^bThis is the lower limit of the validated range as given in reference 6 and is not necessarily the lower limit of detection.

PHOSGENE

Phosgene (COCl_2) is a colorless, low-boiling liquid. At room temperature and 760 mm pressure, it is a colorless gas. Impurities may cause discoloration of the product from pale yellow to green. Phosgene has a characteristic odor, and the odor of the gas can be detected only briefly at the time of initial exposure. At 0.5 ppm in air, the odor has been described as pleasant and similar to that of new-mowed hay or cut green corn. At high concentrations, the odor may be strong, stifling, and unpleasant. In general, phosgene is soluble in aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons, organic acids, and esters. It is removed easily from solvents by heating or air blowing, but because of its toxicity, great care must be taken to control its presence in the atmosphere (1). To prevent the occurrence of pulmonary edema from phosgene exposure, the American Conference of Government Industrial Hygienists established a TLV of 0.1 ppm (2).

Colorimetry, gas chromatography, and infrared spectrophotometry have shown promise of attaining the sensitivity required to detect levels of phosgene below its present TLV and of being adaptable to do continuous real-time monitoring for phosgene (3). These three techniques, plus a recently developed paper tape monitor and piezoelectric crystal device, were chosen for development, evaluation, and a side-by-side test under actual field conditions.

A manual colorimetric method is the current NIOSH recommended standard procedure for phosgene in air (4). This method involves the collection of phosgene in midget impingers containing 4,4-nitrobenzyl pyridine (NBP), N-phenylbenzylamine (BA), and diethyl phthalate (DEP). When phosgene is present, this solution produces a red color. The absorbance is determined at 475 nm. Sampling efficiency is 99% or better. Five micrograms of phosgene can be detected; the minimum sample size is 25 L. High sensitivity is the major advantage of this method. Some of the disadvantages of the method include potential interferences, relative change in color formation with various lots of reagents, and the need for frequent calibration checks. The NBP-BA method is not subject to interferences from normal concentrations of chloride, hydrogen chloride, chlorine dioxide, or simple chlorinated hydrocarbons such as carbon tetrachloride, chloroform, and tetrachloroethylene. A slight depression of color density has been observed under high humidity conditions. Other acid chlorides, alkyl and aryl derivatives which are substituted by active halogen atoms, and sulfate esters are known to produce color with these reagents. However, most of these interferences can be removed in a prescubber containing an inert solvent such as "Freon-113" cooled by an ice bath (3).

The NBP-BA method has been adapted for continuous automated use on a Technicon Air Monitor IV autoanalyzer. Sample air is bubbled into a flowing stream of NBP-BA-DEP reagent. During passage through a mixing coil, the reagent absorbs the phosgene, and the colored complex formation takes place. Air bubbles and liquid are then separated, and the developed reagent is passed to the colorimeter where the color absorbance is measured. The estimated detection limit for the automated Technicon method is 0.05 ppm of phosgene in air using 1-cm cells and 0.01 ppm using 5-cm cells. The Technicon Autoanalyzer has great sensitivity but has a long response time. Up to 20 min may elapse before an excursion is noted, or an excursion of short duration may be missed altogether (3).

GC employing an ECD has been used to detect phosgene in air. Priestley (5) employed a GC system consisting of an aluminum column packed with 30% didecyl phthalate on 100/120-mesh GC22 Super Support Heltes, Burghardt, and Bremen (6) reported a similar method for the determination of low concentrations of phosgene. Dahlberg (7) and Kihlman recommended a stainless steel GC column packed with 20% DC-200 on Chromosorb W. Sensitivities down to 1 ppb were achieved with all three GC methods. However, because of the reactivity of phosgene, the GCs required frequent column conditioning and recalibration. Recently, Singh, Lillean, and Appleby (8) used pulse-flow coulometry for the determination of sub-ppb concentrations of phosgene. They demonstrated that it is possible to compensate for column losses by extrapolating to zero retention times in the column, thereby eliminating the necessity for routine calibration. This method requires a special GC equipped with dual ECDs in series. An investigation of a wide series of column materials and packing indicated that a Teflon column packed with Chromosil 310 would give the best recoveries and resolution at all phosgene concentrations (9).

Infrared spectrophotometry (IR) is another approach used to determine phosgene in the atmosphere. Esposito, Lillean, Podalak, and Tuggle successfully used a Miran II IR gas analyzer (Wilks Scientific Corporation, South Norwalk, CT) to detect phosgene (9). They used a wavelength of $11.8\text{ }\mu\text{m}$ (850 cm^{-1}) because it was relatively free from interferences. The blank region at $11.2\text{ }\mu\text{m}$ (890 cm^{-1}) was used as the reference wavelength. The Miran II was set for a slow (8-s time constant) response and the sample set for a 20.25-m path. One advantage of the method is its ability to detect phosgene at levels as low as 0.025 ppm. Because the Miran II is continuously sampling a large cell volume (5.4 L), there is a "lag" time for the instrument to come to a constant reading when a change in concentration occurs. Trichloroethylene has an absorption band at the phosgene sample wavelength with an intensity about one-third of that for phosgene. Other potential interferences include ammonia, dioxane, ethylene oxide, ethylene amine, and some Freons.

A recent development in the area of phosgene monitoring is the U.E.I. Model 7020 paper-tape monitor. A controlled flow of sample air is drawn through the top half of the tape. The bottom half of the tape, used for reference, remains unexposed. The chemically impregnated tape reacts specifically with phosgene to produce a color whose intensity is proportional to the phosgene concentration. As the exposed tape passes to the photometer, two beams of light guided by optics from a common source are reflected off the top (sample) and bottom (reference) halves of the tape and measured photometrically. The resulting reference-corrected signal drives a concentration-level (panel) meter, and an external recorder is used to set off an alarm if a preset phosgene concentration is exceeded. The detection limit for the tape monitor is 0.005 ppm (3).

A piezoelectric quartz crystal coated with methyltrioctylphosphonium dimethylphosphate was found to be a good detector for phosgene in air. The response curve is linear from 5 to 140 μg . One advantage of the method is that the coated crystal can be used for more than six weeks without significant loss in sensitivity, provided that high ammonia concentrations are not encountered. The response to ammonia is irreversible, and if the substrate is exposed to large doses of ammonia, the response to phosgene is irreversible and increases markedly (10).

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SoRI-EAS-86-981
Project 5614/F
(100::25)mmw:aer

TABLE 42. GENERAL ANALYTICAL METHODS FOR THE DETERMINATION OF PHOSGENE

Method No.	Principle	Potential interferences	Analytical detection limit	Typical sample volumes, L	Minimum ^a detectable concentration	References
1	A. Collection in midget impingers containing 4-nitrobenzyl pyridine (NBP), N-phenylbenzylamine (BA), and diethyl phthalate (DEP) B. Colorimetric determination at 475 nm	A. High humidity B. Acid chlorides C. Alkyl and aryl derivatives	5 µg per injection	25	200 µg/m ³	3
2	Determined by the NBP-BA method adapted for the Technicon Air Monitor IV autoanalyzer	NA	NA	NA	40 µg/m ³	3
3	Gas chromatography with an electron-capture detector	A. Compounds with a similar retention time to phosgene	NA	NA	4 µg/m ³	9
4	Infrared spectrophotometry	A. Trichloroethylene B. Ammonia C. Dioxane D. Ethylene oxide E. Ethylene amine F. Freons	NA	NA	100 µg/m ³	9
5	U.F.I. Model 7020 paper-tape monitor	NA	NA	NA	200 µg/m ³	3

^aCalculated from $\mu\text{g}/\text{m}^3 \cdot \frac{P (\text{MW}) (\text{ppb}) (10^3)}{(82.07) I}$

where

p = pressure in atmospheres

MW = molecular weight

82.07 = gas constant in $\frac{\text{cm}^3 \text{ atm}}{\text{deg. mole}}$

I = absolute temperature (K)

REPORT DOCUMENTATION PAGE	1. REPORT NO. SoRI-EAS-86-981	2.	3. Recipient's Accession No.	
4. Title and Subtitle Development of Analytical Methods for Ambient Monitoring and Source Testing for Toxic Organic Compounds: Volume I - Literature Review			5. Report Date October 1986	
			6.	
7. Authors Ruby H. James, Robert E. Adams Michael M. Thomason, H. Kenneth Dillon			8. Performing Organization Rept No.	
9. Performing Organization Name and Address Southern Research Institute 2000 Ninth Avenue South P.O. Box 55305 Birmingham, AL 35255-5305			10. Project/Task/Work Unit No.	
			11. Contract (C) or Grant (G) No. (C) A3-123-32 (G)	
12. Sponsoring Organization Name and Address Air Resources Board State of California P.O. Box 2815 Sacramento, CA 95812			13. Type of Report & Period Covered Final Report 06/05/84 - 10/31/86	
			14.	
15. Supplementary Notes				
16. Abstract (Limit: 200 words) A literature review of the sampling and analysis methods for toxic organic pollutants in air has been completed. The purpose of this review was to provide guidance to the California Air Resources Board (CARB) in the selection of sampling and analysis methodologies for selected toxic organic pollutants in air. Sampling and analysis methods for 38 compounds or classes of compounds were reviewed. Discussions on sampling strategies, sampling methods, analytical methods, determination of detection limits, quality-control and quality-assurance procedures, and validation criteria have been incorporated into the review. A summary of the physical and chemical properties of the compounds of interest also has been included. Methodology developed by the EPA, NIOSH, CARB, other government agencies, and the private sector served as a resource for the review.				
17. Document Analysis a. Descriptors b. Identifiers/Open-Ended Terms 1. Air Sampling and Analysis - Review 2. Sampling and Analysis Methods for Organic Compounds c. COSATI Field/Group				
18. Availability Statement Release Unlimited. Available from National Technical Information Service 5285 Port Royal Rd. Springfield, VA 22161			19. Security Class (This Report) Unclassified	
			20. Security Class (This Page) Unclassified	
			21. No. of Pages 262	
			22. Price	

(See ANSI-239.18)

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(Formerly NTIS-35)
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